Nano-graphene growth and texturing by Nd:YAG pulsed laser ablation of graphite on Silicon

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Abstract. Pulsed laser ablation from a rotating graphite target operating both in vacuum (~10^-5 Pa) and in He sustaining gas (~10 Pa) has been used to grow thin carbon films on Si <100> substrates kept at temperatures from RT to 900 °C. Synchrotron and laboratory X-ray diffraction (XRD), performed at grazing incidence, established the formation of nano-sized graphene structures at higher deposition temperatures (~ 800 ÷ 900°C). When the carbon plume was expanding in vacuum, these structures resulted to be formed by few parallel graphene layers, characterised by an oriented growth along the graphene planes, with the z axis parallel to the substrate. High resolution (HR) cross section TEM images of C nano-structures on grids or in film/Si substrate confirmed both size and orientation of the graphene nano-particles. The presence of He atmosphere in the reaction chamber changes basically the particle nucleation process: a clustering phenomenon of aromatic structures is promoted in the gas phase also at low temperature. The nano-structured particles, however, are characterised by a round shaped morphology and random orientation. The mass density of deposited films, measured by X-ray reflectivity, is also strongly dependent on the experimental settings: films grown in the inert gas show lower density compared to the vacuum deposited ones. The preferential vertically oriented growth of graphene layers in vacuum and high temperature can be explained as a combined effect of different processes under a fast kinetic mode: thermal surface diffusion, in-plane growth of graphene sheets and line source direction of activated carbon species of the laser plume. He deposited samples are characterised by a different nucleation and growth process and a more complex structure.

Keywords: Nd:YAG pulsed laser deposition, He gas effects, nano-graphene growth and orientation, multi-shell fullerenes, carbon onions, grazing incidence XRD, HR-TEM analysis.

1. Introduction

The discovery of fullerenes [1] and carbon nanotubes [2] have recently opened a sort of new area of research in chemistry, physics and materials science. Nano-devices made of carbon nano-structures, with novel outstanding physicochemical properties, are rapidly going to be produced. Some examples are electron field emitters for ultra-thin displays, quantum wires and nano-probes, nano-transistors and gas storage nano-devices [3]. Both fullerenes and nanotubes can be regarded as peculiar curved graphene structures. Pentagonal rings within the hexagonal graphene plane allow
the bucky-ball curvature and the fullerene formation, while a graphene sheet rolling into a cylinder gives rise to carbon nanotubes [4-6]. These structures, in turn, can be also arranged in a “nested” multi-wall shape, thus producing onion-like or nested fullerenes [7,8] and multi-wall carbon nanotubes (MWCNT) [9], respectively. Starting from these fundamental findings many intermediate and ordered carbon nano-structures have been envisaged and prepared for unconventional applications (nano-cones, horns, fibers, petals, etc.)[10-12].

Our research was actually focused on the influence of experimental deposition parameters on nano-structure formation and texturing of thin carbon films deposited by pulsed laser ablation (PLD). Since most electronic properties, like field emission or charge transport, in carbon materials are associated with aromatic basal planes of graphene layers, due to the high mobility of \( \pi \) band electrons and the close proximity of Fermi level [13], a specific control of aromatic layer formation and orientation is required. In our previous works [14] we reported on PLD nano-structured graphite film deposition and on SEM, Raman and angular dependent NEXAFS characterisation [15]. In this paper, we present the results obtained by grazing incidence XRD analysis and HR-TEM. The particle structure, dimension, texturing and spatial orientation have been examined as a function of growth parameters. The mass density evolution of the films with temperature was examined by x-ray reflectivity.

2. Experimental

2.1 Nd:YAG Pulsed Laser Deposition

Samples have been prepared by pulsed Nd:YAG laser ablation (2\textsuperscript{nd} harmonic \( \lambda = 532 \) nm, \( h\nu = 2.33 \) eV, repetition rate \( f = 10 \) Hz, pulse width \( \tau = 7 \) ns, fluence \( \Phi \approx 7 \) J/cm\(^2\), deposition time = 15 min), from a pyrolytic graphite target (purity 99.99 %) in a vacuum chamber. The system was evacuated with a turbo-molecular pump to a base pressure of \( \sim 10^{-4} \) Pa prior to deposition. The films were deposited on Si <100> substrates placed \( \sim 50 \) mm apart from the graphite rotating target. The substrate temperature was varied from RT to 950 °C. At higher temperature a relevant solid-state reaction between the Si substrate and the incoming ionised carbon species gave rise to SiC formation. A set of sample was deposited in a low pressure He atmosphere (\( \sim 10 \) Pa), taking the other process parameters constant.

2.2 XRD and TEM characterisation

XRD measurements at grazing incidence were carried out both by (a) laboratory setting and (b) synchrotron radiation apparatus at the XRD1 beam-line of ELETTRA storage ring (Trieste, Italy). X-ray reflectivity (XRR) measurements were obtained in laboratory. The details of the experiments performed by the laboratory setting and Synchrotron (ELETTRA) setting are widely described in [16]. Transmission Electron Microscopy (TEM) investigations were carried out with the FEI Tecnai F20 microscope operating at 200 kV, equipped with a Schottky source, super-twin objective lens with 0.24 nm point resolution and 0.14 nm information limit for HR imaging. TEM observations and SAED analysis were performed on ion-beam thinned cross-sectioned specimens and on samples obtained by dispersing the C structures on TEM grids.
3. Results

3.1. Vacuum samples

Figure 1a shows the 2θ scans obtained by the lab set up with constant grazing angle of 0.8 deg. The peaks arising from the Si <100> substrate are green shadowed (the substrate scattering means that the signals from the films come from the whole thickness).

![Graph showing XRD 2θ scans](image)

**Fig 1.** a) XRD 2θ scans obtained in laboratory for the vacuum deposited films. b) 2D diffraction patterns obtained at ELETTRA for the same samples.

The inset shows the intensity of a virgin Si in the 2θ range from 70 to 100 deg. At RT only haloes, typical of an amorphous phase, are visible at 2θ ≈ 25 and 40 deg. At higher temperatures (800, 900 and 950°C) the haloes almost disappear and peaks of a 2D graphite-like lattice begin to be observed. The classical notation of the Miller indices (00Ɛ) and (hk) is used [17].

The 2D lattice character is evident from:
1. the low-angle flanks of the bands steeper than those at high angle,
2. the merging of 100 and 101, and 110 and 112 3D crystalline graphite peak pairs into the 10 and 11 bands, respectively.

At 950 °C, peaks from SiC are also visible (the polytype cannot be determined). Their profiles are symmetric, which means the SiC domains are 3D crystals. No 002 reflection from basal planes of graphite appears in the diffraction patterns.

In fig. 1b a series of 2D diffraction patterns obtained at ELETTRA with grazing angle of ~1 deg is presented. Even in this case the signals come from all the film thickness and the intensity streaks and the faint spots are produced by the Si substrate. At RT the pattern agrees with that obtained in laboratory and is mainly originating from an amorphous phase. At higher temperatures the 10 band of the graphite planes is detected as a broad Debye ring (note that the 11 reflection is outside the collection angle of the 2D detector) together with the strongly oriented 002 reflection from parallel graphene sheets. Two lobes of small angle X-ray scattering (SAXS) are also appearing near the
incident beam stop. A spot from SiC is also observed for 950 °C. All the patterns are invariant for any rotation angle of the sample around the $\phi$ axis (perpendicular to the sample plane). This remark and the analysis of the diffraction patterns of the high temperature deposited samples tell us that:

1. at high temperatures ($800^\circ$C ÷ $950^\circ$C) there is a clear evidence of graphite nano-structure formation;
2. the graphene layers are oriented normal to the film, with $\hat{c}$ axis (the normal to graphite basal plane) parallel to the substrate;
3. the $\hat{c}$ axis can assume whichever orientation in the film plane, and any lattice rotation around the $\hat{c}$ axis is possible;
4. the particles responsible for SAXS are elongated along the normal to the film with a lateral correlation length of about 4 nm, probably associated with pores formation during the film growth.

![Figure 2. TEM images of a sample deposited in vacuum at 800°C. Insets at higher magnification.](image)

a) cross section   b) powder on grid.

A comprehensive analysis of the XRD data allowed us a detailed and exhaustive determination of the pores and the C nano-particle dimensions in 3D space [16]. At higher temperatures, the particles tend to be formed by ~ 4 parallel nano-graphene sheets of ~ 7 x 8 nm size and ~ 1.5 nm thickness. The growth is perpendicular to the substrate along the carbon particle flux direction with a regular and periodic porosity inside.

The HR-TEM analysis performed on high temperature deposited films underlined these findings. The cross section of $C_{\text{vacuum}}$ 800°C sample (fig. 2a) is characterised by a neat and ordered interface and the vertical orientation of growing graphene nano-structures is clearly displayed (see inset of fig. 2a). In the HR-TEM image of the nano-structures dispersed on a TEM grid (fig. 2b) the (100) planes of graphene layers (0.21 nm distance) are shown (see inset at higher enlargements of fig.2b).

### 3.2 He atmosphere (15 Pa) samples

The diffraction patterns of samples deposited in He atmosphere at increasing substrate temperatures (RT ÷ 900 °C) are shown in figs. 3a-d. The patterns at low temperatures are characterised by a halo at $2\theta \approx 20\div25$ deg, suggesting the presence of an amorphous phase,
and a strong Debye ring at $20 \approx 11$ deg assigned to C$_{60}$ face-centred cubic fullerene [18]. At higher temperatures (800°C and 900°C), in addition to the C$_{60}$ Debye ring, a faint ring at $20 \approx 43$ deg, corresponding to the 100 reflection from graphene plane (with interplanar spacing of $\sim 0.21$ nm), becomes evident.

The most interesting feature, however, is the wide and intense annular ring at $20 \approx 21$ deg originating from the overlapping of the 002 reflection from graphene layers and the halo of the amorphous phase. Therefore, at RT the films appear as composed by a dominating amorphous matrix embedding some short ordered (trimers mainly) fullerene C$_{60}$ particles. Higher temperatures cause also some nano-graphene particle formation and condensation in this original frame, characterised by “open” and randomly oriented structure.

Corresponding HR-TEM grid pictures are displayed in figs. 4 and 5. The sample grown at RT (figure 4) shows a compact amorphous structure, locally characterised by ordered planes or by “onion”-shaped fullerene structures.

Figure 3. Synchrotron XRD patterns (a-c) and laboratory 20 scans (d) for the He deposited films. In d the three most intense lines of fcc fullerene are shown. The substrate contributions are the same as in figure 2a.

Figure 4. TEM grid image of “onion”-shaped particles of carbon film deposited in He at RT.
The sample deposited at 900°C shows a low density structure made by round-shaped nano-clusters (fig. 5a), frozen in an amorphous phase and characterised by a random orientation and variable distance of parallel graphene layers inside (see the enlarged pictures in fig. 5b,c).

Figure 5. a. TEM image of spherical particles in C film deposited in He at 900 °C. b,c. Different enlargements of spherical particles showing the randomly oriented graphene layers.

The general features of sample deposited at higher temperature partially resemble the high-density carbon “aerogels” obtained at MIT labs by a sol-gel method [19] and partially characterised by a glassy carbon-like structure inside the particle. These data are consistent with the values of film densities, determined by x-ray reflectivity. They resulted to be a little lower compared to the PLD samples deposited in vacuum [17] and decrease considerably with temperature increasing, as shown in fig. 6. Some He incorporation or presence of voids cannot be excluded. However, from SAXS analysis we have no appearance of a regular and ordered porosity as in the vacuum deposited films.

Figure 6. Film mass density vs deposition temperature specular reflectivity measurements.
4. Discussion

Laser vaporisation of graphite is an unbelievably flexible method for selective production of various novel forms of carbon. It has been extensively studied for deposition of functional materials such as diamond-like carbon, ta-carbon, carbon nanotube or carbon clusters including C_{60} and higher genus and multishell fullerenes [20-22]. Depending on different experimental parameters (i.e. laser wavelength and fluence, target-to-substrate distance, substrate temperature, background gas and pressure), different products can be obtained from the ablation plume and deposited on the substrate. In addition, the surface morphology, density, thickness and grain size of grown films show significant dependence on the inert sustaining gas and process pressure. The interaction of laser ablation plumes with a background gas has received increased attention recently due to its importance in pulsed laser ablation and nano-particle formation and growth.

Compared with expansion into vacuum, the interaction of the plume with an ambient gas is a far more complex gas dynamic process, due to the appearance of new physical processes such as deceleration, thermalization of the ablated species, interpenetration, recombination, formation of shock waves and clustering [23].

Above 10 Pa, most of the initial kinetic and internal energy of the plasma plume is quenched by multiple collisions with the ambient gas on its way from the target to the substrate [24-26]. This quenching effect has been exploited by Wood et al. [25] to produce nano-particles with a narrow size range. The expansion of the ablation plume into an ambient background resulted in shock waves due to a sort of “ploughing” of the plume as it propagates through the gas [24]. Multiple collisions were able to dissipate the kinetic energy of the ablated species until they slow sufficiently to nucleate and form nano-clusters in the shock fronts. Spatial and temporal brevity of these shock fronts ensures that the range of cluster sizes is small. Helium, being the lighter gas compared to Ar or N_{2}, gives rise to rapid “cooling” of hot electrons and to an enhanced clustering phenomenon of the carbon plasma plume. This is why it is preferred as a buffer for the preparation of fullerenes and other carbon nano-structures [25]. The He pressure in the range 1÷10 Pa was chosen in our experiments as the optimal condition for nano-particle formation according to the work of Harilal [27]. Carbon films produced by pulsed laser deposition are wavelength dependent. Irradiation of graphite with 532 nm results in the ejection of small carbon ion clusters (e.g. C_{3}^{+}, C_{5}^{+}, C_{7}^{+}, C_{9}^{+}) with kinetic energy between 30 and 50 eV. Graphitic films are then produced by large, slow carbon species. Recently a room temperature C_{60} formation has been reported by means of a CO_{2} laser vaporisation in He [21].

In our experiments, using a 532 nm pulsed laser source, at pulse length 7 ns and fluence Φ~7 J/cm^{2}, in vacuum, we grew amorphous film at room temperature. As the substrate temperature increases, the structure of the films gradually changes from an amorphous network to an organised structure composed by particles of nano-sized dimensions embedded in an amorphous matrix, as detected by XRD analysis. Owing to a mobility enhancement of reactive species with temperature and to the Wulff dynamic construction, a peculiar aromatic clustering occurs. The activated carbon species saturate the sp^{2} dangling bonds of the graphene planes, rapidly growing along the plume flux direction, i.e. perpendicular to the Si substrate. The sharp preferred orientation of the 002 XRD reflection and HR-TEM cross section analysis clearly show that the graphene planes are oriented perpendicular to the substrate surface, with the normal to the aromatic basal plane, ê, parallel to the <Si> substrate.

The structure of films deposited in He ambient is mainly controlled and determined by collisions and “quenching” of the plume species by He gas. A loss of kinetic energy and a partial “gas phase condensation-nucleation” of nano-clusters take place. The inert gas is also affecting the macroscopic spherical shape of the particles, the lower film density and the random orientation of graphene
layers in nano-structures formed at higher temperatures. No regular porosity has been detected. However, the very low density at high T can be tentatively explained by some inclusion of He atoms mainly when a high turbulence at the substrate level can be generated by fast thermal induced absorption-desorption process of pristine generated small clusters. We think that in this phase another process takes also place: some of the small clusters in the plasma act as nuclei for larger complex construction and self-assembling of carbon hyper-structures, as multishell fullerenes, “onions-shaped” and polyhedral graphite nano-particles [22]. The final structure is characterised by few local ordered C_{60} dimers or trimers, multishell fullerenes, polyhedral graphite particles and some parallel nano-graphene layers merged in an amorphous matrix. At RT the film density is quite higher and the structure is mainly constituted by small C_{60} particle in a predominantly amorphous structure. Some “onions” are also shown in the grid HR-TEM analysis. However, as a general comment, it has to be taken into account the well known effects of electron irradiation, mainly during the HR-TEM analysis, on carbonaceous material inducing the transformation of graphitic polyhedra into spherical onions, as a minimal energy configuration of large carbon clusters [8,20], but also some structure formation; in particular, the irradiation-induced transformation of graphitic nanoparticles into diamond [28,29].

5. Conclusion

We studied the influence of different experimental conditions on the final structure of carbon films deposited by PLD from a poly-crystalline graphite target. The texture of deposited nano-structures depends both on the substrate temperature and the presence of an inert sustaining gas. The structure of the vacuum deposited films changes with temperature, from a random amorphous network to nano-graphene ordered particles of increasing size.

From the XRD and HR-TEM analysis, the dimensions and spatial orientation of the graphene particles are evident: few parallel graphene layers, with a lateral correlation length of ~ 4 nm, grow oriented normal to the substrate and to the film plane. Films deposited in a He atmosphere show different shapes. They are characterized by an amorphous structure and the presence of fullerenes, irrespective of substrate temperature. Increasing temperature, the film structure is characterised by a very low density and round shaped nanoparticles, made of polyhedral graphitic layers, onions or multishell fullerenes. This decrease probably can be explained by some inclusion of He atoms and more complex, open and disordered carbon structures, recently studied and proposed by Harris[30].

The particles do not show either correlation length or orientation with respect to the film plane and the average size is weakly dependent on temperature increase. In comparison with the vacuum deposition, the presence of a background gas, introduces an additional parameter of nonlinear dynamics, thus leading to a more unpredictable self-organised final structure, due to the extreme complexity of the generated chaotic processes.

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7. References

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