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Control of cluster synthesis in nano-glassy carbon films

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Abstract

Carbon films were prepared by pulsed laser deposition (PLD), changing buffer gas nature and pressure and laser power density. Nanometer-sized cluster assembled (CA) films, resulting from direct aggregation of carbon clusters in the ablation plume, were obtained. Visible Raman spectroscopy shows that all films are trigonally co-ordinated and structurally disordered, with a dependence of the degree of disorder on the deposition parameters. The microstructure and morphology of the films were studied in a complementary way by scanning electron microscopy (SEM) both in plane and in cross-section, and by atomic force microscopy (AFM). Different growth modes are found in the deposited CA films, depending on the interplay of laser fluence and nature-pressure of the buffer gas. Threshold fluences of increasing value separate dense columnar growth from sponge like morphology, from an open dendritic structure. AFM pictures show that our glass-like carbon films consist of agglomerates of nanometer-sized clusters. Cluster formation in the plume is modeled, allowing to estimate the average number of carbon atoms per cluster. The calculated size of the clusters depends mainly on ambient gas pressure. Cluster sizes obtained by model predictions agree with those directly observed by transmission electron microscopy (TEM) imaging and with the deduced film coherence length from Raman spectroscopy conducted herein.

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1. Introduction

Carbon displays a wide variability of structures and properties. Besides crystallizing in several forms, there are many non-crystalline carbon forms due to the different possible types of bonding and different degrees of disorder. The versatility of carbon materials is due to the critical dependence of their physical properties on the sp^2 (graphite-like) to sp^3 (diamond-like) bond ratio [1]. Many types of sp^2 bonded carbons are known, with different degrees of graphitic order that range from microcrystalline graphite to glassy carbon. Any amorphous carbon has a mixture of sp^3, sp^2 and occasionally sp^1 bonds, possibly in the presence of a fraction of hydrogen. Each modification of the relative abundance of each type of hybridisation is associated to a change of the density of states and of the energy gap. Over the last 20 years pulsed laser deposition (PLD) has demonstrated to be a versatile technique to synthesize carbon films in vacuum, or at low buffer gas pressure, whilst controlling the hybridisation, the degree of structural disorder and the extent of clustering of sp^2 phase. Diamond-like carbon (DLC) films with well-differentiated structural, mechanical, optical and electronic properties were deposited [2]. By contrast, scarce attention was devoted to the synthesis in a *high*-pressure inert gas, of cluster-assembled (CA) carbon films [3], whose molecular structure depends on the conditions of cluster formation and coalescence onto the substrate.

Here the morphological and structural properties of carbon films pulsed laser deposited in inert gas atmosphere at

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high pressure are reported. Ablation of carbon atoms and ions from the irradiated target, plasma formation and interaction of the plume of ejected particles among themselves and with buffer gas strongly modify the microstructure and structure of the deposited films. We performed scanning electron microscopy (SEM) and atomic force microscopy (AFM) to investigate film morphology, whilst visible Raman spectroscopy was employed to study carbon atom co-ordination and film crystallinity.

The mechanisms leading to the synthesis of carbon clusters in the ablation plume are discussed and the deduced cluster sizes are compared with transmission electron microscopy (TEM) observations and Raman spectroscopy results.

2. Experimental details

The films were deposited at room temperature on cleaned Si(1 0 0) substrates, starting at a base pressure of 10^{-4} Pa, in helium, or argon at pressures $p_{He;Ar} = 0.6$, 30, 50, 60, 70, 250, 10^3 and 2×10^3 Pa. Highly oriented, high purity (99.99%) pyrolytic graphite (HOPG) was ablated with laser pulses from a KrF excimer laser ($\lambda = 248$ nm, pulse duration $\tau = 20$ ns, repetition frequency 10 Hz, incidence angle 45°), at power densities ranging from 8.5 to 19 MW mm^{-2}. The average deposition rate of films ranged from around 0.7 nm s^{-1} in helium to around 0.8 nm s^{-1} in argon. We used a JEOL JSM 6300 SEM, with the primary beam accelerated at 15 keV and an incidence angle of 30°. After metallization, both surface and cross-section pictures were taken for all examined samples. A 'Thermo Microscopes CP Research' AFM instrument was used in non-contact mode, at room temperature, in ambient air. Unpolarised visible macro-Raman spectra were recorded in backscattering geometry with 532 nm excitation from a Nd:YAG laser using a Jobin-Yvon T64000 triple grating spectrometer with a resolution of 1 cm^{-1}.

3. Results

Both planar and cross-section SEM observations of CA films deposited in helium show columnar, nodule-like and dendritic, highly porous microstructures. These structures are found in the above sequence, mainly as a function of increasing buffer gas pressure in the deposition chamber p_{He} and also, less sensitively, of the deposited power density. For various combinations of power density and helium pressure, nodes develop within the columnar structure during film growth. At the lowest $p_{He} = 0.6$ Pa, the smooth and laterally homogeneous film surfaces are similar to those of diamond-like carbon (DLC) films deposited in vacuum. In Figs. 1(a) and (b) is shown the typical evolution of film microstructure with increasing p_{He}. At medium-low p_{He} (30–70 Pa) spherically capped nodes, partly agglomerated with each other, are embedded in densely packed columns (Fig. 1(a)). Film-substrate adhesion is good. With increasing p_{He}, the number density (cm^{-3}) of the nodes

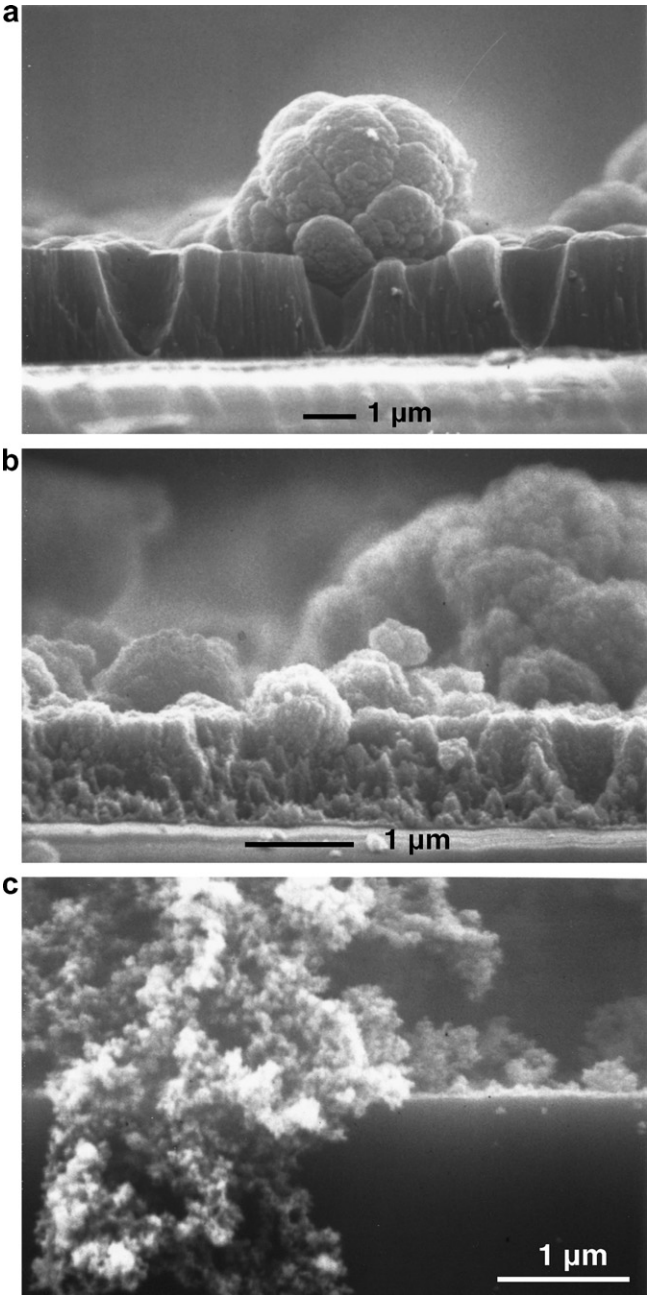

Fig. 1. SEM cross-sections of representative CA carbon films. (a) $p_{He} = 60$ Pa, $P = 16$ MW mm^{-2}; (b) $p_{He} = 250$ Pa, $P = 8.5$ MW mm^{-2}; (c) $p_{Ar} = 2$ kPa, $P = 16$ MW mm^{-2}.

increases while their cap radius reduces. The ratio between measured node diameters, at the top and at one half of node height is equal, or very close to $2^{1/2}$; the ratio between the diameter at one half of node height and that at one fourth of node height is unchanged. Such diameter ratios correspond to parabolic node shape; they hold for all nodes well resolved in all CA films deposited at $p_{He} = 50$, 60 and 70 Pa. The result differs from the conical shape predicted by purely ballistic growth models where the ratio of node diameters scales with $n^{1/2}$, n being an integer greater than 2 [4].