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Synthesis of carbon nitride thin films by low-energy ion beam assisted evaporation: on the mechanisms for fullerene-like microstructure formation

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Abstract

Carbon nitride (CN_x) thin films were grown at different substrate temperatures by low-energy (<100 eV) ion beam assistance deposition (LE-IBAD) in order to discern possible formation mechanisms of a fullerene-like (FL) microstructure. The samples are compared to those of well-structured FL-CN_x films synthesized by reactive magnetron sputtering (MS). The comparison yields similar trends for both techniques, such as limitation of the nitrogen content at 20–25 at.%, dominance of sp^2 hybrids, as well as thermally activated chemical desorption of C_xN_y species from the substrate during growth. However, CN_x films produced by LE-IBAD are amorphous. The lack of FL structural features correlates with a lower degree of sp^2 clustering, attributed to the promotion of nitrile groups. Therefore, low-energy ion bombardment is shown not to be a sufficient condition for the growth of FL-CN_x. This result reinforces the eventual relevance of pre-formed C_xN_y species at the sputtering target in MS for the introduction and/or evolution of FL arrangements.

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1. Introduction

Fullerene-like (FL) carbon nitride (CN_x) is a solid phase that consists of bent and cross-linked nitrogen-containing graphite basal planes of nanoscale dimensions [1]. This atomic arrangement results in a compliant and tough thin film material, making it a promising candidate for tribological applications [2]. So far, well-structured FL-CN_x has been mostly synthesized by reactive magnetron sputtering (MS), while, recently, pulsed laser deposition (PLD) resulted also in somewhat structured films [3]. Low-energy (<100 eV) ion bombardment has been shown to be essential for the synthesis of FL-CN_x thin films [2] together with moderate substrate temperatures (200–500 °C) [4]. These growth conditions are necessary to increase mobility and reactivity at the surface but also to enable selective etching via chemical desorption of volatile C_xN_y species from the film surface [5]. In addition, low-energy ions are also required to avoid excessive re-sputtering of the growing film and ion-induced damage (amorphisation) on the microstructural evolution [4].

Despite the successful synthesis of FL-CN_x, the growth mechanisms leading to this atomic arrangement are still not fully understood. In this sense, the role of N incorporation in

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the film structure is crucial. The most common model for the evolution of FL-CN_x assumes the introduction of substitutional N in graphene sheets, where the curvature results from the formation of N-induced structural defects such as pentagons [6] and/or basal-plane corrugation [7]. In this context, it would be expected that, at the required substrate temperatures, N incorporation during growth by means of low-energy N ions would be sufficient for the evolution of FL-CN_x. However, in addition to the role of atomic species, C_xN_y ($x,y \leq 2$) moieties emitted from the sputtering target during MS deposition might also be determinant for the microstructure development [8]. In this alternative approach, the microstructure evolution has to be understood as the interplay between arriving and desorbing species. The presence of preformed C_xN_y precursors in the film-forming flux has been established for reactive MS [8] and PLD [9,10], which indicates their eventual importance in the growth process of FL-CN_x.

In order to discern the mechanisms leading to FL arrangements, the study of CN_x films synthesized by different growth techniques and the role of film-forming species is necessary. In contrast to MS and PLD, ion beam assisted deposition (IBAD) provides independent sources for C and N precursors and the presence of preformed C_xN_y species does not take place. Therefore, CN_x films synthesized by low-energy IBAD (LEIBAD) in this work provide alternative information about the role of film-forming species and effects of the ion bombardment on the FL structure evolution. The results show that the use of independent C and N atomic fluxes by LE-IBAD does not yield FL structures, thus, reinforcing the proposed growth model driven by the presence of C_xN_y precursors [8].

2. Experimental details

2.1. Sample preparation

CN_x thin films were grown onto Si(100) substrates by LE-IBAD at a base and working pressure of $\sim 10^{-4}$ and 3×10^{-2} Pa, respectively. The carbon atoms were provided by electron-beam evaporation of graphite with evaporation fluxes at the substrate between 1 and $2 \cdot 10^{15}$ atoms/cm^2 s. The simultaneous N ion bombardment assistance at low-energy was performed with an End-Hall ion source. In this type of ion gun, the ion energy corresponds to approximately 60% of the anode voltage, with a dispersion of ~30% [11]. In this way, ion energies in the range of 40–60 eV were used by adjusting the anode voltage between 60 and 100 V. The ion beam current (~85% N_2^+ and ~15% N^+ [12]) is proportional to the anode current, providing current densities at the substrate between 40 and 120 μA/cm^2 for anode currents between 0.5 and 2.0 A. In order to mimic the conditions for fullerene-like (FL) CN_x in MS deposition [2], the substrate temperature was varied from RT to 500 °C.

Well-structured FL-CN_x samples were grown as reference material by DC reactive magnetron sputtering of carbon in a N_2/Ar atmosphere at a substrate temperature of 450 °C. The synthesis was performed at a total working pressure of 0.4 Pa, negative substrate bias of 25 V and various N_2/Ar gas mixtures. A more detailed study of these samples can be found elsewhere [5]. The discussion is focused on the sample grown at 100% N_2 for better comparison with the growth conditions by LE-IBAD, although it does not yield the most curved FL features. However, the results can be generalized for all the FL-CN_x samples prepared by MS.

2.2. Sample characterization

The composition of the films was studied by elastic recoil detection analysis (ERDA). The measurements were performed with 35 MeV Cl^{7+} ions impinging at an angle of 15° relative to the film surface. The backscattered ions and the recoils are detected with a Bragg-Ionization chamber placed at a scattering angle of 30°. Additionally, a standard Si solid barrier detector (ORTEC®) was located at a scattering angle of 20° for hydrogen detection. In this case, an aluminum foil was employed to stop heavier recoils and backscattered Cl^{7+} ions.

Micro-Raman spectra were collected with a Renishaw Ramascope 2000 microspectrometer at an excitation wavelength of 514.5 nm. The power density on the sample was below 5 GW/m^2 to avoid unintentional modification of the bonding structure of the samples (confirmed by repetitive measurements on the same sample position). The spectral resolution achieved with this system is 1 cm^{-1} and the spectral slit width is 4 cm^{-1}.

Spectroscopic ellipsometry (SE) measurements were done within the probing photon energy range of 0.7–4.0 eV. The spectral behavior of the ellipsometric parameters, Δ and Ψ, was acquired in the autoretarder mode [13] of a variable angle spectroscopic ellipsometer (VASE) (J.A. Woolam, USA). The WVASE® software was used for data acquisition and processing. The SE data was simulated using a three-phase model (air/CN_x/Si). A general parametric function model based on the Kim and Garland approach [14] is used to describe and fit the optical constants for CN_x layers. The mathematical details of this model are discussed elsewhere [15]. Such an approach provides dielectric function values, which are consistent with Kramers-Kronig relations. The validity of the fitting results was established by comparing the fitted values with the real thickness as measured by transmission electron microscopy (TEM).

Cross-sectional specimens for high-resolution transmission electron microscopy (HRTEM) were made by gluing slices of the samples film-to-film into the windows of Ti discs followed by mechanical thinning and polishing. Finally, the discs were thinned to electron transparency by ion beam milling [16] with a 10 keV Ar^+ ion-beam at an