Chemical and physical sputtering effects on the surface morphology of carbon films grown by plasma chemical vapor deposition

Luis Vázquez\textsuperscript{1(a)} and Josephus G. Buijnsters\textsuperscript{2,b)}

\textsuperscript{1}Instituto de Ciencia de Materiales de Madrid (CSIC), CSor Juana Inés de la Cruz 3, 28049 Madrid, Spain
\textsuperscript{2}Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

(Received 18 May 2009; accepted 25 June 2009; published online 6 August 2009)

We have studied the influence of chemical and physical sputtering on the surface morphology of hydrogenated carbon films deposited on silicon substrates by bias-enhanced electron cyclotron resonance chemical vapor deposition. Atomic force microscopy based power spectrum density (PSD) and roughness analysis have been used to investigate the film morphology. This study has been possible due to the appropriate choice of the experimental variables, in particular, gas mixture, resulting in either nitrogen-free (a-C:H) or nitrogenated carbon (a-CN:H) films, and substrate bias \((V_b)\). Under these conditions, chemical sputtering is present for a-CN:H deposition but it is negligible for a-C:H film growth, while physical sputtering processes appear for both systems for \(V_b \approx -85\) V. When physical sputtering does not operate, the film growth with simultaneous chemical sputtering leads to a characteristic a-CN:H granular surface morphology. Furthermore, PSD analysis reveals that a spatial correlation of the a-CN:H film surface roughness, up to distances \(-300\) nm, becomes a fingerprint of the coexistence of growth and chemical erosion processes on the film morphology. However, once physical sputtering takes place, the influence of chemical sputtering by reactive nitrogen species on the final surface morphology becomes negligible and both a-CN:H and a-C:H film morphologies are ultrasmooth. © 2009 American Institute of Physics. [DOI: 10.1063/1.3184349]

I. INTRODUCTION

An accurate control of the surface morphology and roughness of plasma deposited thin films is of crucial importance in many technological applications. For instance, in the production of microdevices and magnetic storage media there is a strong need for ultrasmooth, thin, and hard films as functional layers or protective overcoats. On the other hand, rough surfaces generally display an enhanced hydrophobicity,\textsuperscript{12} which might be a prerequisite in many biomedical applications. Therefore, the characterization and study of the film surface roughness is important to assess the influence of the film growth processes on the film morphology. In this sense, the measurement and quantification of the roughness and its corresponding lateral correlations through the surface roughness power spectrum analysis have been proven to be important for understanding fundamental phenomena as well as technological processes.\textsuperscript{2} In addition, the surface growth dynamics is a characteristic of both the deposition technique and process conditions applied during the film growth, therefore, its study can reveal us the roughening and/or smoothening mechanisms operating for a given system as functions of deposition parameters. This has been demonstrated successfully for materials such as hydrogenated amorphous silicon (a-Si:H) deposited by thermal activation of silane,\textsuperscript{3} silica films deposited by chemical vapor deposition (CVD),\textsuperscript{4} and plasma-grown, hydrogenated amorphous carbon (a-C:H).\textsuperscript{5}

Over the past decades the mechanical, tribological, optical, and electronic properties of a-C:H films have been explored intensively. Due to the combination of the high hardness, high wear resistance, low friction, chemical stability, and biocompatibility, the highly versatile, hard diamondlike carbon materials that are generally produced by plasma CVD or physical vapor deposition have already been incorporated in numerous applications. In addition, the use of a-C:H overcoats in the magnetic recording industry gained specific interest during the past decade.\textsuperscript{6} The incorporation of nitrogen into the amorphous carbon film microstructure\textsuperscript{1} is attractive since it directly influences the tribological resistance, wettability, and electroconductivity of the synthesized material, but it can also promote the formation of fullerene-like structures displaying outstanding mechanical properties.\textsuperscript{7}

In nuclear fusion research, carbon is used on plasma facing components and appears unequalled due to its superior thermomechanical properties. Nevertheless, erosion of the carbon material by atomic hydrogen and energetic species from the fusion plasma limits the lifetime of the components and eventually dilutes the plasma with impurity ions.\textsuperscript{9} Therefore, many studies have been elaborated to gain a more detailed and fundamental understanding of the chemical erosion by thermal and ionic hydrogen alone,\textsuperscript{9,10} and in combination with a simultaneous bombardment of energetic noble ions such as Ar\textsuperscript{+} and Ne\textsuperscript{+}.\textsuperscript{11-13} Although significant progress has been achieved to elucidate the underlying
mechanisms leading to the hydrocarbon release and to quantify the erosion rates, surprisingly, few studies have been devoted to analyze the effects of chemical sputtering on the thin film morphology evolution.

This is also the case for the study of chemical erosion induced by nitrogen species. From a theoretical point of view, it is worth to cite the 1+1 statistical models developed by Aarão Reis and Franceschini for carbon-nitrogen film growth. From the experimental perspective, Freire Jr. et al. investigated the surface modifications of a-C:H films when exposed to a nitrogen rf plasma and found an abrupt increase in surface roughness when treated at a self-bias voltage of 100 V. For lower and higher bias voltages the surface was significantly less affected by the nitrogen bombardment. However, due to the complex and generally broad ion energy distribution (IED) of the applied rf plasma, no firm conclusions about the mechanism of chemical erosion by nitrogen ion bombardment could be drawn from the observed trend. In this respect, the application of a dc self-bias directly to the substrate can be a more efficient method to change the ion energy without significantly changing the plasma parameters, especially in the case of electron cyclotron resonance (ECR) plasmas. It is known that the IED of argon and methane ECR plasmas at pressures above 0.15 Pa is very narrow with a full width at half maximum in the order of several eV. In this way, sharp transitions or threshold behaviors as a function of the ion energy are more easily distinguished.

During plasma growth of hydrogenated carbon nitride (a-CN:H) films, two different processes are taking place simultaneously, i.e., film formation and etching of the growing surface. Whereas the formation process is mainly controlled by the content of carbon-containing species, the etching can be ascribed to the highly reactive nitrogen atoms. The latter process is generally referred to as chemical sputtering since it involves chemical reactions between target and projectile atoms thereby forming species which are more loosely bound to the surface and more easily sputtered. This process depends on both the kinetic energy and chemical reactivity of the impinging species. On the contrary, physical sputtering causes the ejection of target atoms by the direct momentum transfer of impinging projectiles to target atoms. Physical sputtering takes place for all target materials and incident particles if the energy is higher than a certain threshold value, typically in the range of about 100 eV.

In this work, we address the study of the influence of chemical and physical sputtering processes on the surface morphology and roughness of carbon films grown by ECR-CVD. On one hand, the existence of chemical sputtering is determined by the chemical nature (i.e., reactivity) of the incoming species. Here, we have deposited amorphous carbon films from argon-methane gas mixtures, with and without an additional input of nitrogen gas, in order to study two growth systems, with appreciable and negligible chemical sputtering, respectively. In the former case, we produce nitrogenated hydrogenated amorphous carbon (a-CN:H) films whereas in the second one nitrogen-free, hydrogenated amorphous carbon (a-C:H) coatings are obtained. It should be noted that in our system chemical sputtering is mainly caused by the action of nitrogen species since nitrogen has a good mass match to carbon and atomic nitrogen has a strong chemical activity. In addition, atomic nitrogen is readily formed within our plasma and further the bombarding N$_2^+$ ions even supply two nitrogen atoms per incoming nitrogen ion. The chemical sputtering of other ions in combination with atomic H, such as Ar$^+/H$, could, in principle, play a role in our film growth as well. However, this is less effective due to the nonreactivity of Ar and the relatively low atom-to-ion-flux (H/Ar$^+$). On the other hand, physical sputtering processes are triggered once the energy of the incoming ions is above a threshold value. For the case of carbon films, Ar$^+$ and N$_2^+$ ion-induced physical sputtering takes place for $V_b$ more negative than about −85 and −100 V (Refs. 23 and 14, respectively). Accordingly, in order to control the contribution of each process we have varied, from 0 down to −300 V, the dc self-bias applied to the substrate. Therefore, we are able to address the influence of chemical and physical sputtering processes on the surface morphology of ECR-CVD carbon films by studying the dependence of the morphology of a-CN:H and a-C:H films with the external bias.

II. EXPERIMENTAL

A. Film deposition

a-C:H and a-CN:H films were deposited by bias-enhanced ECR-CVD (ASTeX, mod. AX4500). Gas mixtures of argon/methane [20/13 SCCM (SCCM denotes cubic centimeter per minute at STP)] and argon/methane/nitrogen [20/13/3 SCCM] were applied for the a-C:H and a-CN:H films, respectively. The two-zone deposition reactor consists of a plasma chamber in which an argon or an argon-nitrogen plasma is formed under resonance conditions, which in turn is connected to an adjacent chamber in which methane is introduced and where the actual film deposition takes place under remote plasma conditions. The reactor was operated with a 2.45 GHz microwave plasma source at 205–210 W input power using a constant operating pressure of 1.4 × 10$^{-2}$ mbar. Double-side polished p-type silicon (100) with a thickness of 280 μm was used as substrate material. To systematically vary the ion energy, a dc self-bias ($V_b$) varying from −300 to 0 V (floating bias) was directly applied to the silicon substrates while no intentional heating was employed. As already discussed in earlier works, the use of a dc bias might result in a lower effective bias in the case of growing insulating a-C:H films. However, independent IR and Raman spectroscopy analyses did not show any changes in microstructure for layers up to 2–3 μm. Due to the much thinner films considered here (three times thinner, see below), shielding of the applied dc voltage can be discarded. The film growth rate for the sampled bias window varied between 0.21 and 0.28 and 0.13–0.17 nm s$^{-1}$ for the a-C:H and a-CN:H films, respectively. Due to this difference the deposition time for a-C:H film growth was fixed at 1 h, whereas a growth time of 2 h was selected for the a-CN:H films. Under these conditions, the film thickness resulted to be similar and larger than 600 nm for all cases. At the end of each deposition run the substrate temperature was evaluated by a thermocouple attached to the substrate holder. It was
found that the substrate temperature progressively increased going from floating bias to $-300$ V dc self-bias, but it was always lower than $140$ °C.

B. Film characterization

The film surface morphology was analyzed ex situ by atomic force microscopy (AFM). The measurements were made with a Nanoscope IIIa (Veeco) equipment operated in tapping mode and using silicon tips with a nominal radius of 10 nm. Different areas of each sample were studied. It should be stressed that in this study we have studied the influence of the deposition conditions on the film morphology. For that purpose we have analyzed films with similar thickness and characterized their roughness and, in particular, the roughness lateral correlations. Obviously, a deeper insight into the mechanisms governing the growth dynamics is achieved when studying both the so-called static and dynamic growth exponents. This kind of study is now in progress. However, in this work in order to characterize the surface roughness correlations we have used the radially averaged power spectral density (PSD) that is defined as $PSD(k, t) = \langle H(k, t) H(-k, t) \rangle$, where $H(k, t)$ is the Fourier transform of the surface height function $h(r, t)$ that represents the local surface height at position $r$ and time $t$, $k$ being the spatial frequency in the reciprocal space. The operator $\langle \cdots \rangle_k$ represents the average over all $k$ vectors with the same modulus. The corresponding PSD curves and roughness values were obtained with the AFM software. The surface roughness correlations can be identified in a logarithmic plot of the PSD curve versus $k$ by the existence of linear regions that are not parallel to the $x$-axis. In these regions the scaling relationship $PSD \propto k^{-2(\alpha+1)}$ is obeyed, where $\alpha$ is known as the roughness scaling exponent. This exponent describes the spatial correlations of the surface roughness. The existence of a surface roughness correlation within a given length scale implies that the interface growth at two given surface sites within this length scale is not independent.

III. RESULTS AND DISCUSSION

A. Dependence of the $a$-C:H and $a$-CN:H surface film morphology on $V_b$

In Figs. 1(a)–1(f), representative AFM images of the $a$-C:H films obtained for different applied substrate biases are shown. From zero bias down to $-80$ V the films basically are morphologically similar since they all display a cauliflower-like topography consisting of relatively large and rounded aggregates of smaller, nanometer sized grains. These films display similar roughness and grain aggregation with an average aggregate size of 55–65 nm. However, at $-90$ V the morphology drastically changes: It becomes smoother (note the smaller $z$-scale for Fig. 1(d)) and a granular structure with a lateral size of $\sim 40$ nm appears. This smoothening process is further enhanced when the bias becomes even more negative. Figures 1(e) and 1(f) show very flat surfaces obtained after 1 h of $a$-C:H growth at $-150$ and $-250$ V, respectively. These films are as flat as the silicon substrate, without any glimpse of a granular structure.

The change in the $a$-CN:H surface morphology with the externally applied bias is shown in Figs. 2(a)–2(f). For bias values above $-80$ V, the film morphology, even at zero bias, is not cauliflower-like. Instead, a marked granular morphology develops with an average size of $\sim 50$ nm. However, the film is not smooth since height fluctuations between grains are observed [note the high/bright and low/dark zones in Fig. 2(a)]. As the bias becomes more negative, down to $-60$ V, the clear granular structure remains with a similar size, in the 50–60 nm range, and the film roughness increases slightly as the bias becomes more negative [Fig. 2(b)]. At $-80$ V [Fig. 2(c)] the film morphology is still granular but the grains start to show some sort of aggregation leading to larger structures and consequently higher roughness. From bias values in the $-90$ to $-300$ V range, a behavior similar to that found for the ultrasmooth $a$-C:H films is retrieved [Figs. 2(d)–2(f)]. This smoothening of the morphology, regardless of the type of film, induced when high negative biases are applied, is clearly observed from Fig. 3. Here, the root-mean-square (rms) surface roughness values for both the $a$-C:H and $a$-CN:H films are displayed as a function of the applied sub-

![FIG. 1. (Color online) 1 \times 1 \, \mu m^2 \, AFM \, images \, of \, a-C:H \, films \, grown \, in \, a-C:H \, films \, grown \, for \, 1 h \, on \, Si \, substrates \, with \, an \, external \, bias \, of: \, 0 \, V (a), \, -50 \, V (b), \, -80 \, V (c), \, -90 \, V (d), \, -150 \, V (e), \, and \, -250 \, V (f). The vertical \, bar \, corresponds \, to \, 35 \, nm (a), \, 31 \, nm (b), \, 32 \, nm (c), \, 13 \, nm (d), \, 1.2 \, nm (e), \, and \, 1 \, nm (f), \, respectively, \, as \, marked \, in \, each \, figure.](image1)

![FIG. 2. (Color online) 1 \times 1 \, \mu m^2 \, AFM \, images \, of \, a-C:H \, films \, grown \, for \, 1 h \, on \, Si \, substrates \, with \, an \, external \, bias \, of: \, 0 \, V (a), \, -50 \, V (b), \, -80 \, V (c), \, -90 \, V (d), \, -150 \, V (e), \, and \, -250 \, V (f). The vertical \, bar \, corresponds \, to \, 29 \, nm (a), \, 31 \, nm (b), \, 54 \, nm (c), \, 16 \, nm (d), \, 1.6 \, nm (e), \, and \, 1 \, nm (f), \, respectively, \, as \, marked \, in \, each \, figure.](image2)
substrate bias voltage. The films grown under $V_b < -90$ V show a rms roughness in the 0.1–0.2 nm range irrespective of the composition of the gas mixture.

B. Ultrasmooth morphology for films grown under physical sputtering conditions

The comparison of the surface topographies of these two growth series shows that both film morphologies are rather similar for $V_b < -85$ V while they differ greatly for $V_b > -85$ V. Physical sputtering effects can operate above a certain ion energy threshold. For carbon films, this threshold energy is ~85 eV for Ar$^+$ ions and ~100 eV for N$_2^+$ ions. Obviously, in both systems ultrasmooth film morphologies are produced once physical sputtering is operative (Table I). In previous studies on similar ultrasmooth film growth systems in which relatively high energetic ions were employed the extreme low roughness of the resulting films was explained on the basis of the existence of thermal spikes or ion-induced enhancement of the surface mobility of the precursor species weakly bound to the film surface. In the latter case a net downhill current of material would be induced, which tends to smoothen the surface morphology leading to the observed surface ultrasmoothness. Additionally, it is well known that under these bias conditions the ion bombardment leads to denser films. Indeed, we did find that the flat films of both types, grown at $V_b < -85$ V, resulted to be smoother and denser than those grown at less negative biases.

TABLE I. Summary of the experimental systems and bias conditions studied. For each case, the operative sputtering processes as well as the observed surface morphologies are indicated.

<table>
<thead>
<tr>
<th>System</th>
<th>Bias</th>
<th>Physical sputtering</th>
<th>Chemical sputtering</th>
<th>Film surface morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-C:H</td>
<td>$&gt; -85$ V</td>
<td>No</td>
<td>Negligible</td>
<td>Cauliflowerlike and rough with a single scaling regime</td>
</tr>
<tr>
<td>a-C:H</td>
<td>$&lt; -85$ V</td>
<td>Yes</td>
<td>Negligible</td>
<td>Flat and featureless</td>
</tr>
<tr>
<td>a-CN:H</td>
<td>$&gt; -85$ V</td>
<td>No</td>
<td>Yes</td>
<td>Granular with two scaling regimes (roughness correlations)</td>
</tr>
<tr>
<td>a-CN:H</td>
<td>$&lt; -85$ V</td>
<td>Yes</td>
<td>Yes</td>
<td>Flat and featureless</td>
</tr>
</tbody>
</table>

Further insight on this induced ultrasmooth morphology can be obtained from the corresponding PSD curves. In Fig. 4 the PSD curves of the a-C:H and a-CN:H films grown at $V_b = -200$ V are shown. Clearly, both curves practically overlap and are characterized by a single scaling regime with $\alpha \sim 0$, which extends from 20 up to 600–800 nm. This scaling behavior, together with the analysis of the corresponding growth exponent, was previously found to be consistent with the Edwards–Wilkinson growth mode. From these data, the similarity in terms of roughness and roughness correlations is evident between a-C:H and a-CN:H films grown for $V_b < -85$ V, i.e., when physical sputtering operates. In principle, physical sputtering of the grown films can be induced by all types of bombarding ions, such as Ar$^+$, N$_2^+$, and even C$_m$H$_n^+$, but for our remote plasma deposition conditions physical sputtering will mainly be determined by either Ar$^+$ or Ar$^+$/N$_2^+$. It is worth noting that the physical sputtering effects determine the film ultrasmooth morphology in both systems, regardless of the existence of nitrogen induced chemical sputtering processes. Moreover, the additional N$_2^+$ ion bombardment for the a-CN:H films does not seem to alter the behavior found when rather mainly Ar$^+$ ions impinge on the growing a-C:H interface. This fact is understandable because of the relatively small amount of nitrogen compared to that of Ar in the gas mixture.

C. Film growth without physical sputtering

As commented before, for $V_b > -85$ V physical sputtering is practically absent. In this bias range both film morphologies differ clearly. This could be associated to the different contributions of chemical sputtering during the growth of a-C:H (negligible) and a-CN:H (appreciable) films. In order to better understand the growth processes determining the film morphology (Table I), we will analyze these systems separately.

1. Diffusion-limited growth without chemical sputtering processes

As Fig. 1 shows, all a-C:H films grown in this voltage range do show a cauliflower morphology (Table I) characterized by the agglomeration of smaller nanometer grains. In principle, such morphology is consistent with that expected for standard CVD growth systems where thermal precursor
species diffuse following an isotropic angular distribution across the gas phase to impinge at various angles on the growing interface where they react in order to stick to it (with a given sticking probability). Under this scenario, incoming precursor species will have a higher probability to impinge on higher surface sites (protrusions) than in lower ones (valleys or depressions) leading to shadowing effects. This growth behavior would favor the formation of aggregates at the protruding film areas and, therefore, would lead to rough surfaces.\textsuperscript{32,33}

In order to obtain a better insight into the dependence of the film morphology on bias for both systems, it is useful to analyze their PSD curves. For $V_b \geq -80$ V, the PSD curves of the a-C:H films (Fig. 5(a)) practically overlap and show a single correlated regime with $\alpha \sim 1$ for length scales shorter than $\sim 65$ nm, which corresponds to the average size of the large cauliflower-like aggregates. The overlapping of the PSD curves indicates that the a-C:H film morphology does not change appreciably with the external bias for $V_b \geq -85$ V. This is important since the incoming Ar$^+$ ions could enhance the formation of dangling bonds at the film surface, which would lead to an increment of the sticking coefficient of the impinging radical growth precursors.\textsuperscript{34,35} The energy required for these processes is close to 2 eV.\textsuperscript{23} Additionally, the incoming ions could also induce an enhanced mobility of the precursor species weakly bound to the film surface as commented above.\textsuperscript{28,29} The extent of these processes could increase, in principle, with the applied bias. In any case, from our results it is clear that the influence on the a-C:H film morphology of such Ar$^+$-induced processes does not change markedly within this bias range.

2. Diffusion-limited growth with simultaneous chemical sputtering

The a-CN:H film morphologies for $V_b > -85$ V (Fig. 2(a)–2(c)) are markedly different from those observed for the a-C:H films (Figs. 1(a)–1(c)). The a-CN:H films are rather granular, especially for $V_b > -80$ V, with evident height fluctuations between grains (Table I). The aggregation of these small nanometer structures, which was characteristic of the a-C:H films produced in this bias range, is not longer observed. These differences could, in principle, be associated to the occurrence of chemical sputtering effects during the diffusive growth process characteristic of CVD described above. As noted above, at $-80$ V the film is granular but some grain aggregation is already observed.

The corresponding PSD curves [Fig. 5(b)] are characterized by two scaling regimes that can be identified by the existence of two linear regions with a crossover length of $\sim 50$ nm ($k_c \sim 0.017$ nm$^{-1}$). The first scaling regime with $\alpha_1 \sim 1$ clearly corresponds to the roughness correlations inside the grain whereas the second one, with $\alpha_2 < \alpha_1$, is due to the correlations for distances from the grain size up to even $\sim 300$ nm. The existence of this roughness correlation implies that the film height (i.e., growth) at a given surface site is not independent of those at sites distant even $\sim 300$ nm. From Fig. 5(b) it is also evident that the slope of the second regime (i.e., the $\alpha_2$ value) increases as $V_b$ becomes more negative.

Figure 6 displays the $\alpha$ values found for both types of films. As explained before, a single $\alpha$ value, close to 0, is obtained when $V_b < -85$ V for both systems. The bias range of interest is $V_b > -85$ V for which a-C:H films present $\alpha_1$ values close to 1. A similar behavior is found for the $\alpha_2$ values of a-CN:H films, although in this case $\alpha_2$ reaches higher values for the less negative biases. However, as noted above, the great difference between both films consists in the

FIG. 5. PSD vs $k$ plots for a-C:H (a) and a-CN:H (b) films grown for 1 and 2 h, respectively, at 0 V (○), $-50$ V (□), and $-80$ V (▲). In (a) the main scaling behavior with $\alpha = 1$ is indicated. In (b) the crossover $k_c$ value between the two scaling regimes is marked.

FIG. 6. Plot of the $\alpha$ values as a function of the applied substrate bias for the a-C:H (■) and a-CN:H films (open symbols). For the nitrogenated films two values of $\alpha$ are displayed, i.e., $\alpha_1$ (○) and $\alpha_2$ (□), which correspond to the two observed scaling regimes. The error bars are not plotted when they are smaller than the symbol size.
existence of a second roughness scaling regime for the a-CN:H films characterized by a second roughness exponent, \( \alpha_2 \). As Fig. 6 shows, \( \alpha_2 \) increases from values close to 0.3 at zero bias up to about 1 for an external bias of \(-80 \text{ V}\) where \( \alpha_2 \) becomes closer to \( \alpha_1 \), which agrees with the small aggregation observed under this bias condition [Fig. 2(c)]. The second scaling regime appears clearly for biases less negative than \(-80 \text{ V}\), which is the range in which chemical sputtering operates but physical sputtering does not.

This analysis indicates that the existence of the second scaling regime (\( \alpha_2 \)), only observed for the a-CN:H film growth, appears when chemical sputtering operates. Clearly, this regime is not observed when physical sputtering dominates (Fig. 4) or when neither physical nor chemical sputtering processes take place [Fig. 5(a)]. Particularly interesting is the growth condition at floating bias (\( V_b=0 \text{ V}\)) for which physical sputtering processes clearly do not operate. Obviously, for such condition the observed differences in the surface morphology between the a-C:H [Figs. 1(a) and 5(a)] and a-CN:H [Figs. 2(a) and 5(b)] systems should originate directly from the role played by the nitrogen gas that is added to the gas mixture in the case of a-CN:H film growth.

In general, the electron temperature in an Ar/N\(_2\) plasma is much higher than in a pure Ar plasma. In addition, energetic neutral nitrogen species such as excited molecular nitrogen (N\(_2^+\)), N\(_2\), and metastable N\(_2\) are produced not only close to the ECR excitation chamber but also in the late expansion of the plasma\(^{16}\) and these nitrogen species can reach the growing film surface with energies of a few eV. Although their incoming energy is relatively low, they are able to produce chemical sputtering processes at the growing interface during a-CN:H growth.\(^{14,21}\) This interpretation is consistent with the smaller growth rate observed without bias for the a-CN:H films (~8 nm/min) compared to that of a-C:H coatings (~12.5 nm/min) since such species are not present for a-C:H deposition. Then, this result already indicates the implications of chemical sputtering effects on the surface morphology, film roughness, and roughness correlations.

In order to further verify the appearance of a second, long-range, roughness correlation regime associated to chemical sputtering effects, we did design and perform the following experiment. First, we grew an a-C:H film for 1 h on a Si substrate and then we added nitrogen to the gas mixture and continued the growth for 1 h. In Figs. 7(a)–7(c) are displayed the characteristic morphologies of a-C:H films grown for 1 h [sample A (a)] and 1+1 h [sample B (b)] and a film grown for 1 h under a-C:H conditions and 1 h further under a-CN:H conditions [sample C (c)]. Clearly, for cauliflowerlike morphologies [Figs. 7(a) and 7(b)] the roughness is defined by the steep slopes of the large protrusions. Their lateral size increases from ~65 nm [Fig. 7(a)] to ~115 nm [Fig. 7(b)] with the deposition time. In contrast, the a-C:H/a-CN:H film [Fig. 7(e)] is smoother and its roughness shows two characteristic lengths: (i) the individual ~50 nm grain (small structures clearly observed on the surface); (ii) the average distance between next main minima of height [i.e., between dark spots in Fig. 7(c)].

The corresponding PSD curves are shown in Fig. 7(d). Both a-C:H curves overlap for high k values and show a single scaling regime, with \( \alpha \sim 1 \), connected to the cauliflowerlike aggregate morphology. The scaling region extends to smaller k values for the film deposited for 2 h in agreement with the roughening and coarsening of the cauliflowerlike morphology with deposition time. In contrast, the a-C:H/a-CN:H film shows again two scaling regimes: The first one for high k values corresponds to the grain structure whereas the second one, with \( \alpha_2 \sim 0.5 \), is related to the height differences between them. This regime extends up to length distances of ~200 nm. This \( \alpha_2 \) value agrees with the local jagged surface morphology observed in Fig. 7(c).\(^{37}\) It is worth noting that the PSD of sample C lies below those of samples A and B for \( k \geq 0.005 \text{ nm}^{-1} \) (i.e., distances smaller than 200 nm), which indicates that chemical sputtering smoothens the starting rough film surface.

From these analysis and experiments, we can clearly conclude that at least for our system, the existence of a second scaling regime, as assessed by PSD analysis of AFM data, is a fingerprint of the coexistence of chemical sputtering and growth processes during the film deposition.

D. Chemical sputtering induced roughness correlations

A thorough understanding of the existence of a second scaling regime spanning up to ~300 nm becomes rather complicated because of the simultaneous operation of growth
and sputtering processes that can have different synergisms between them. However, its origin cannot be based on surface relaxation processes considered in the model by Araão Reis and Franceschini\textsuperscript{15,16} because of the large correlation length.

This second scaling regime is observed when both growth and chemical sputtering processes take place simultaneously. On one hand, growth processes are associated to diffusive processes in the gas phase. The precursor species will have an isotropic distribution and will impinge preferentially on surface protruding areas, leading to the presence of shadowing effects during the growth process. As shown above, this growth scenario results in the aggregated cauliflowerike morphology for \( V_b = -80 \) V.

On the other hand, chemical sputtering is caused by the impingement of nitrogen species on the growing film surface. These incoming etching species have, roughly, two different incoming angular geometries. On one hand, there are uncharged reactive species (i.e., radicals and excited molecules) with an isotropic angular distribution. They will follow incoming pathways similar to those of the radical growth species. On the other hand, nitrogen ions will be accelerated by the external bias toward the substrate surface. Accordingly, they will tend to follow ballistic trajectories, with an increasing orientation along the normal to the substrate surface, as the bias increases.\textsuperscript{18} Due to the effective displacement of carbon atoms in near subsurface regions by nitrogen, a high density of broken bonds will be created at or very close to the surface.\textsuperscript{21,39} These broken bonds can react with atomic hydrogen forming volatile hydrocarbon species and can also chemically interact with the decelerated nitrogen atoms producing thermal volatile \( \text{C}_3\text{N}_2 \) or \( \text{C}_3\text{N}_2\text{H}_2 \) species\textsuperscript{40} that could then be re-emitted.

Particularly interesting is the morphology obtained for the a-CN:H film at 0 V. Under this condition, the incoming chemical sputtering species will have an isotropic distribution and will follow random trajectories before impinging on the film surface. Therefore, they will arrive preferentially at surface protrusions. This incoming geometry implies shadowing effects for both the radical growth and chemical sputtering species. However, it should be noted that shadowing growth effects lead to unstable (i.e., rough) interfaces while shadowing etching (erosion) processes result in smoother surfaces.\textsuperscript{31,42} Therefore, under this bias condition chemical sputtering and growth processes have opposite effects on the film surface morphology. For this condition the film surface is already characterized by a PSD displaying two scaling regimes and the difference between \( \alpha_1 \) and \( \alpha_2 \) is the most pronounced.

As the bias becomes more negative, but higher than \(-90\) V, the contribution of nitrogen ions to chemical sputtering increases. As noted above, these ionic species will present an increasing anisotropic distribution as the bias becomes more negative.\textsuperscript{38} In addition, the number of incoming nitrogen ions will increase with the applied bias. Therefore, the relative weight of ion species (reaching the surface mainly vertically) with respect to those uncharged species (isotropic diffusive trajectories) on chemical sputtering will increase with the bias. Then, as the bias becomes more negative, the contribution of shadowing (i.e., smoothening in this context) effects in chemical sputtering will be lessened. Accordingly, the surface smoothening associated to chemical sputtering caused by uncharged species decreases in agreement with the increase in the a-CN:H film roughness and \( \alpha_2 \) value for decreasing bias from 0 to \(-90\) V.

It is worth noting that recently the apparition of two roughness scales was reported for the plasma etching of silicon surfaces.\textsuperscript{43} This behavior was explained on the basis of the coexistence of etching and growth processes (i.e., etching inhibitor events) during the surface dynamics. Also, the different angular distributions and sticking probabilities of the etching and growth species were key factors to explain the development of a dual nanoscale roughness. Likewise, the observed development of a surface morphology with two scaling regimes when chemical sputtering and diffusive growth processes coexist can be due to the interplay of erosion and growth mechanisms.

Nevertheless, it should also be kept in mind that the (re)-emission of the species involved in chemical sputtering could correlate (i.e., connect) surface sites relatively distant from each other leading to growth correlations. Besides, the thermal species involved in chemical sputtering processes can have largely varying sticking probabilities.\textsuperscript{44} In addition, hydrogen atoms and radicals arriving at the growing interface can block the available growth sites leading to lower sticking coefficients.\textsuperscript{16,45} Due to this low effective sticking the re-emitted product species can survive many collisions at the growing film surface before being finally redeposited on it. Therefore, they will also be transported to areas that have no direct line of sight with the surface location of sputtering.\textsuperscript{21,46} In this redeposition process the specific surface morphology will also play a role. For instance, species desorbed at surface depressions could be redeposited more likely on the growing surface than those desorbed at surface protrusions.

Finally, we would like to stress the complexity of the ECR-CVD growth system due to the different processes occurring simultaneously and showing different synergisms. For instance, sticking probabilities play a crucial role in the final film morphology\textsuperscript{32} and their values depend on many parameters such as the \( \text{Ar}^+ \) ion bombardment, concentration of atomic hydrogen, energy and angle of impact of reactive radicals,\textsuperscript{44} and internal vibrational energy of the precursors to cite a few. In any case, we think that our study shows the interest to analyze experimentally the film surface roughness and particularly the surface correlations. Also, there is a clear necessity of developing theoretical approaches and simulations on the influence of physical and chemical sputtering processes on the film surface morphology.

\textbf{IV. CONCLUSIONS}

We have studied the influence of physical and chemical sputtering on the growth of carbon films by ECR-CVD by designing the growth system conditions adequately. Thus, we have grown a-C:H and a-CN:H films (by changing the gas mixture composition) for which chemical sputtering is negligible and appreciable, respectively. For both systems the
growth species have an isotropic angular distribution leading to shadowing effects. Additionally, we have varied the substrate bias potential, $V_b$, from 0 down to $-300$ V as physical sputtering only operates for $V_b < -80$ V. By this appropriate choice of the experimental conditions we have been able to identify the influence of both sputtering processes on the film morphology.

(i) Physical sputtering leads to ultrathin films regardless of the existence of nitrogen induced chemical sputtering. This extreme film surface flatness is likely produced by the enhancement of the surface mobility of the precursor species induced by the energetic impinging ions.

(ii) When physical and chemical sputtering do not operate, the carbon film morphology, which does not change with $V_b$, is cauliflowerlike and relatively rough. In addition, the corresponding PSD only shows a single scaling region. This morphology is consistent with the shadowing effects inherent to diffusion-limited growth systems such as CVD.

(iii) In contrast, when physical sputtering does not operate but chemical sputtering does, the film morphology changes markedly since it becomes granular without grain aggregation. The film surface has two scaling regions: The first one associated to the granular structures and the second one, which can extend up to $\sim 300$ nm, is likely related to the interplay between simultaneous growth and erosion processes although some contribution from re-emission of the species involved in chemical sputtering cannot be discarded.

ACKNOWLEDGMENTS

Financial support is acknowledged from the Spanish Ministerio de Educación y Ciencia (MEC) Grant No. FIS2006-12253-C06-03 and Consolider-Ingenio under Grant No. CSD2007-00010. J.G.B. acknowledges the support of the Dutch NWO Veni grant. We thank R. Cuerno, M. Castro, and M. Nicol for fruitful discussions.