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Growth of carbon nanocone arrays on a metal catalyst: The effect of carbon flux ionization

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The growth of carbon nanocone arrays on metal catalyst particles by deposition from a low-temperature plasma is studied by multiscale Monte Carlo/surface diffusion numerical simulation. It is demonstrated that the variation in the degree of ionization of the carbon flux provides an effective control of the growth kinetics of the carbon nanocones, and leads to the formation of more uniform arrays of nanostructures. In the case of zero degree of ionization (neutral gas process), a width of the distribution of nanocone heights reaches 360 nm with the nanocone mean height of 150 nm. When the carbon flux of 75% ionization is used, the width of the distribution of nanocone heights decreases to 100 nm, i.e., by a factor of 3.6. A higher degree of ionization leads to a better uniformity of the metal catalyst saturation and the nanocone growth, thus contributing to the formation of more height-uniform arrays of carbon nanostructures.


I. INTRODUCTION

Arrays of vertically aligned high aspect ratio nanostructures, such as nanorods, nanocores, and nanotubes demonstrate outstanding characteristics that make them attractive for various applications, such as nanoelectronic devices, electron emitters, and gas sensors. In the fabrication of such arrays, the ultimate goal is to achieve the highest level of the ordering and size uniformity of the individual nanostructures within the entire pattern. In most cases, the arrays of vertically aligned nanostructures should be made of highly conductive materials and be placed on a conductive substrate to sustain a high electron field emission current from the sharp tips with a curvature radius of several nanometers. From this point of view, carbon nanostructures on doped silicon substrates are often considered as one of the most promising choices of a suitable material system.

The process of the carbon nanostructure array growth on the surface may be conditionally divided into three main stages. During the first stage (catalyst pattern formation which is achieved by metal deposition on the substrate surface), carbon material is not supplied to the surface. During the second and the third stages, i.e., the metal catalyst nanoparticle saturation with carbon and the carbon nanostructure growth, carbon species are supplied to the substrate surface from the process environment. During these stages, carbon precursors are dissolved in the metal nanoparticles since carbon ions and atoms are usually delivered to the metal nanoparticles directly from the process environment, as well as from the substrate surface by adatom diffusion. The nanostructure nucleation process is triggered as soon as the catalyst nanoparticles get saturated with carbon.

In the synthesis of dense arrays of vertically aligned carbon nanostructures, plasma based methods, such as plasma-enhanced chemical vapor deposition (PECVD) are among the most perspective techniques. It has been convincingly demonstrated that the use of low-temperature plasma environments results in much more uniform and simultaneous saturation of the metal catalyst nanoparticles used for catalyzing the nanostructure growth, thus enabling a simultaneous nucleation and development of the carbon nanostructures at early growth stages. In this paper we analyze, using a complex numerical Monte Carlo/surface diffusion technique, the growth of nanocone arrays on the surface in neutral and plasma environments, and pay special attention to the stages 2 and 3, i.e., the growth of the nanocones on the saturated metal nanoparticles. It is shown that the use of the low-temperature plasma provides a narrower distribution of the nanocone heights, i.e., results in the growth of a more height-uniform array of the carbon nanocones. Besides, we demonstrate that nanocone arrays with much smaller maximum nanocone heights can be synthesized in a low-temperature plasma environment. Moreover, the use of highly ionized carbon fluxes provides the formation of the nanocone arrays of higher quality, in terms of their size uniformity which determines the electron emitting and other size-dependent characteristics. Therefore, the variation of the plasma parameters (specifically, the degree of ionization of the carbon flux) turns out to be a convenient tool for controlling the nanostructure array characteristics.

In this article, we report on a complex numerical simulation of the nanoarray growth by modeling the three main physical phenomena that play a key role in the nanostructure formation: diffusion of adsorbed carbon atoms on the substrate surface, saturation of metal catalyst with carbon, and sputtering of the growing nanocones with carbon ions impinging from the plasma. The first two important effects, namely the surface diffusion and the catalyst saturation, have been studied in detail in our previous works which were mainly devoted to the initial stages of the nanostructure growth. At the further stages of growth, when the nanostruc-
ture heights become large enough to play a role in the redistribution of the electric field near the surface, the third key phenomenon, namely, the sputtering of the nanostructures should be taken into account. In this article, this important effect is systematically taken into account.

The article is structured as follows: In Sec. II, we present the details of the numerical model and simulation routines. In Sec. III, the main results of our numerical simulations are summarized. Section IV is devoted to the discussion and interpretation of the results of our numerical experiments. The main results of this work are summarized in Sec. V.

II. MODEL

In this work, we have adopted the following scenario for the formation and growth of the nanocone array. First of all, we have assumed that the nucleation of the carbon nanostructures is possible only on the carbon-saturated metal catalyst nanoparticles, and the nanostructures cannot nucleate and grow on the “free” surface of the substrate, as well as on nonsaturated nanoparticles. Thus, the growth of carbon nanocones proceeds through several stages: formation of an initial pattern of ultrasmall metal catalyst nanoparticles; then, the saturation of this pattern with carbon material; and finally, the growth of nanocones on the saturated nanoparticles. In the model, we do not consider the formation of the metal nanoparticles (which involves the different physical mechanisms and hence different modes, like those described in Ref. 19) and mainly concentrate on the saturation and growth stages that are characterized by the supply of carbon precursors to the surface (in contrast to the metal nanoparticle formation stage when the carbon is not supplied but the metal is deposited).

During the saturation and growth stages of our interest here, carbon species are deposited on the surface to effect the saturation of the catalyst nanoparticles and the growth of the nanocones on the nanoparticles that were saturated. In this case, carbon precursors are predominantly deposited on the substrate surface between the catalyst nanoparticles (we consider the low surface coverage case which is typical for carbon nanocone arrays), then they diffuse on the surface to the nanoparticles, dissolve in the catalyst, and the catalyst material eventually reaches the saturation point. Upon the catalyst material saturation, a nanostructure nucleate on the top of the catalyst nanoparticle, presumably, due to the local oversaturation is caused by the additional carbon atoms deposited on the nanoparticle. Upon the nanocone nucleation on the saturated catalyst nanoparticles, the nanocone nuclei grow by simultaneously increasing their height and the base radius. The main reason for setting the height nonuniformity is most likely due to nonsimultaneous saturation of the metal nanoparticles. During the final stage, the nanocones continue growing until the moment of catalyst poisoning; this process is outside the scope of this work. It is important to stress that during the growth the nanocone sputtering is one of the key shape-determining processes.

As it was said above, the process of formation of the catalyst pattern is not considered here. In our numerical experiments, we consider a system consisting of a biased substrate with the metal (specifically, nickel) catalyst particles and the growing nanocones, immersed in a low-temperature plasma environment. A low-temperature plasma of suitable characteristics can be produced by various methods, e.g., by inductive and capacitive radio frequency discharges,16 cathodic20 and anodic26,27 vacuum arcs, and microwave discharges.28

The effect of carbon sputtering on the growth and shaping of carbon nanocones was quantified in this work by taking into account the dependence of the sputtering yield on the energy and angles of incidence of the impinging species. A strong increase of carbon sputtering at angles of incidence approaching 90° (measured with respect to the normal to the surface, i.e., at grazing angles) has previously been reported for Ar and metal ions.20-31 Quite similar effects also take place in the sputtering of diamond.32 A very important observation is that the ion reflection at angles of incidence exceeding 85° (carbon on carbon) were not observed when the ion energies were lower than 300 eV, i.e., in the practically important case. On the other hand, the sputtering yield does not exceed 0.6–0.7 for low energies.33 At energies lower than 50 eV, the sputtering proceeds through the chemical route and the angular dependence is almost negligible.34 It was also demonstrated that under oblique ion incidence the materials feature a low sticking coefficient and enhanced self-sputtering.34

The processes described in our model are shown in Fig. 1. We consider the deposition of carbon ions onto the substrate, catalyst particles, and nanocones. The flux of carbon atoms is distributed uniformly about the entire surface of the substrate. The ion motion between the plasma bulk and the catalyst nanoparticles with the growing nanocones on them is determined by the electric field. It is assumed that the ions enter the plasma sheath with the Bohm velocity where $m$ is the carbon ion mass, and $T_e$ is the electron temperature. The case of a thin sheath (i.e., the case of the substrate at floating potential or at low bias) is considered. Thus, the sheath width can be estimated as where $\lambda_D = k_B T_e/n_e$, where $\lambda_D$ is the Debye length, $k_B$ is a constant.
of the order of $1^{35}$, $e$ is the electron charge, $e_0$ is the dielectric constant, and $n_c$ is the electron density in the plasma.

The ion trajectories in the vicinity of the nanocones were calculated using the Monte Carlo (MC) technique. The details of the MC simulations are described elsewhere.$^{36,37}$ The distribution of the ion flux on the substrate surface between the nanocones was used to calculate the diffusion fluxes to the catalyst nanoparticles. For this purpose, we used the surface diffusion equation$^{38}$

$$\frac{\partial n}{\partial t} = D_s(x,y) \left( \frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} \right) + \Psi_D - \Psi_E - \Psi_A,$$  

where $D(x,y)$ is the surface diffusion coefficient, $n$ is the surface density of carbon adatoms, $\Psi_D(x,y)$ is the deposition flux of atoms and ions to the substrate surface, $\Psi_E(x,y)$ is the evaporation flux from the substrate surface, $\Psi_A(x,y)$ is the flux of carbon adatoms to the catalyst nanoparticles on the surface, and $(x,y)$ are the Cartesian coordinates. The deposition flux to the substrate surface $\Psi_D(x,y)$ is calculated by the above described MC technique. In this model, we did not consider the carbon ion collisions with the carbon adatoms on the surface, since the probability of such collisions is low. The evaporation flux $\Psi_E(x,y)$ is determined by the evaporation rate equation

$$\Psi_E = \eta \nu_0 \exp(-e_d/kT_S),$$  

where $e_d$ is the energy of adatom evaporation from the substrate surface, $k$ is Boltzmann's constant, $T_S$ is the surface temperature, $\nu_0$ is the frequency of lattice atom oscillations. The surface diffusion coefficient used in Eq. (1) was taken in the form

$$D_s = \frac{\lambda_S^2 \nu_0}{4} e^{-e_d/kT_S}.$$  

The growth of the carbon nanocones was modeled by the length equation

<table>
<thead>
<tr>
<th>Parameter, dimension</th>
<th>Notation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean radius of catalyst nanoparticles, nm</td>
<td>$R_m$</td>
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</tr>
<tr>
<td>Carbon nanocone height range, nm</td>
<td>$H_m$</td>
<td>0–2500</td>
</tr>
<tr>
<td>Number of nanocones</td>
<td>$N$</td>
<td>2000</td>
</tr>
<tr>
<td>Mean spacing between nanocones, nm</td>
<td>$\lambda_n$</td>
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</tr>
<tr>
<td>Electron temperature in the plasma, eV</td>
<td>$T_e$</td>
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</tr>
<tr>
<td>Ion energy at the sheath edge, eV</td>
<td>$e_i$</td>
<td>2</td>
</tr>
<tr>
<td>Gas temperature, °C</td>
<td>$T_g$</td>
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</tr>
<tr>
<td>Gas pressure, Pa</td>
<td>$P_g$</td>
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</tr>
<tr>
<td>Substrate bias, V</td>
<td>$U_b$</td>
<td>50</td>
</tr>
<tr>
<td>Substrate area, $\mu m^2$</td>
<td>$S_b$</td>
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</tr>
<tr>
<td>Carbon flux to substrate, ML×s$^{-1}$</td>
<td>$\Psi_0$</td>
<td>0.1</td>
</tr>
<tr>
<td>Number of carbon ions in Monte Carlo simulations, $-$</td>
<td>$N_i$</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Surface temperature, °C</td>
<td>$T_s$</td>
<td>600</td>
</tr>
<tr>
<td>Time of deposition, s</td>
<td>$t_d$</td>
<td>up to 2500</td>
</tr>
<tr>
<td>Frequency of lattice atom oscillations, s$^{-1}$</td>
<td>$v_0$</td>
<td>$3.5 \times 10^{13}$</td>
</tr>
</tbody>
</table>

FIG. 2. Distributions of nanocone lengths for the neutral gas process with the deposition time $t_d$ as a parameter. Weakly ionized carbon flux ($k_i=0.05$), $t_d=100$ s (a), $t_d=300$ s (b), $t_d=500$ s (c), $t_d=1000$ s (d), and $t_d=2500$ s (e). Electron temperature $T_e=2$ eV, carbon influx $\Psi_E=0.1$ ML/s.
The Monte Carlo technique was used to simulate the ion motion towards the surface system comprising approximately 2000 nanocones. An initial position of each ion was randomly chosen at the sheath boundary, with the ion velocity equal to the Bohm velocity. During the simulation, the coordinates of the ion impact on the substrate surface were recorded, and thus the microscopic topography of the ion current over the surface was obtained. Besides, we have also recorded the coordinates of ion impact on the nanocone surface, and thus the ion flux to the nanocone surface from the plasma was obtained. The flux of carbon atoms sputtered from the nanocone surface $\varphi_{i,S}$ was calculated using the sputtering coefficient and the ion flux to the nanocone surface from the plasma.

Equation (1) was solved numerically to calculate the carbon adatom balance on the surface and finally to calculate the fluxes of carbon precursor to the borders of each catalyst nanoparticle. As boundary conditions for Eq. (1), we used, first, the set of equations for the adatom re-evaporation fluxes $\varphi_{r,e}$ from the boundaries of catalyst nanoparticles to the two-dimensional adatom vapor on the surface

$$\varphi_{r,e} = \frac{\pi d_i}{\lambda_m} \nu_0 e^{-\varepsilon_{d,S}/kT_s},$$

where $\varepsilon_{d,S}$ is the surface diffusion activation energy for the desorption of carbon atoms from the boundary of the catalyst nanoparticle to the two-dimensional adatom vapor on the substrate surface. Second, we assumed that the carbon adatom density at the boundary of the simulation domain is equal to the mean carbon adatom density throughout the whole surface. Then, we have calculated the kinetics of the catalyst nanoparticle saturation and carbon nanocone nucleation using the technique described in detail elsewhere.40,41

The surface simulation domain was 2000 × 2000 nm, with 2000 initial (nonsaturated) catalyst nanoparticles placed randomly. We have used an experimental catalyst pattern as a model for constructing the catalyst pattern used in the simulation. The list of the main simulation parameters is shown in Table I.

III. RESULTS

The main results of our numerical experiments are shown in Figs. 2–7. Specifically, Figs. 2–4 illustrate temporal dependencies of the distributions of nanocone lengths for the neutral, weakly ionized, and highly ionized process environments, respectively, with the deposition time $t_d$ as a parameter. The time evolution of the nanocone pattern is presented in the form of bar charts, with the total number of carbon...
nanocones $N_{CN}=2000$. Each bar represents a group of the nanocones with the length difference not exceeding 5 nm.

From these figures one can see that the time evolution of the nanocone ensemble changes dramatically with the ionization degree. The distribution function of the carbon nanocones grown from the neutral gas environment is wide and comprises nanocones with the lengths ranging from zero to 300 nm, as shown in Fig. 2. With the flux ionization coefficient $k_i=0.25$ (Fig. 3), the distribution function becomes narrower; the nanocones shorter than 50 nm are absent, and the number of the nanocones with the length of around 100 nm (corresponding to the distribution peak) increases. With the high ionization coefficient $k_i=0.75$ (Fig. 4), the distribution becomes very narrow, without the nanocones less than 150 nm and higher than 250 nm.

It can also be noted that the distribution function has a similar shape in all the three cases considered, namely the position of the distribution peak is located in the first third of the nanocone length range. Nevertheless, there is a clear difference between the nanocone length distribution shown in Fig. 2 (neutral gas-based) and the distributions shown in Figs. 2 and 3. Indeed, in the array grown in the neutral gas process the nanocones of a very small length are still present even after a long (2500 s) time of deposition. On the contrary, in the plasma-based process, short nanocones are absent. One can thus introduce an additional parameter—the minimum nanocone length $L_{\text{min}}$ which actually is zero for the neutral gas process (Fig. 2) and $L_{\text{min}}=50$ nm for $k_i=0.25$, and $L_{\text{min}}=125$ nm for $k_i=0.75$.

The dependence of the width of the nanocone length distribution $\delta_W$ on the deposition time with the carbon flux ionization degree as a parameter is shown in Fig. 5. The width of the distribution increases with time for all $k_i$, reaches 360 nm for the zero ionization, and only 100 nm for the highest ionization coefficient $k_i=0.75$ considered here. At the initial moment of deposition, the rates of the distribution widening are the same for all ionization degrees, as it is seen efficient $k_i=0.75$ (Fig. 4).

FIG. 5. Dependence of the width of nanocone length distribution $\delta_W$ on deposition time with the carbon flux ionization degree as a parameter. The inset corresponds to the catalyst saturation stage and reveals a strongly nonlinear dependence of the width of the nanocone length distribution due to the different kinetics of the catalyst saturation in the plasma environments with different degrees of ionization of carbon precursor fluxes.

FIG. 6. Dependence of the maximum nanocone height on time with the carbon flux ionization degree as a parameter. The inset corresponds to the catalyst saturation stage. In the highly ionized flux case the maximum nanocone height decreases for 100 s of the start of deposition due to strong sputtering of the highest nanocones.

FIG. 7. (Color online) 3D visualization of carbon nanocone patterns grown on Ni catalyst particles, after incubation time $t_i=2500$ s, on substrate fragment $500 \times 500$ nm, total flux of carbon material $\Psi = 0.1$ ml/s. The maximum length shown is 2000 nm, carbon flux with ionization degree $k_i=0.75$ (a) and $k_i=0.0$ (b).
from the same angle of the curve inclination in the graph. Then, with the nanocones growing, the rates change. Besides, a close examination reveals an interesting point. In the neutral gas-based process, the width of the distribution increases almost linearly with time in the entire time range; in the highly ionized flux case, this dependence demonstrates a clearly visible plateau, which means that the nanocone pattern develops without any widening of the distribution. An inset in Fig. 5 illustrates the saturation which occurs at 500 nm; with the distribution width exceeding 1000 nm, \( \delta_{W} \) for the highly ionized flux process starts increasing again but with the rate noticeable lower than the rates in other cases considered.

Figure 6 shows the results of calculations of the maximum nanocone height \( L_{\text{max}} \) as a function of time, with the flux ionization degree as a parameter. The \( L_{\text{max}} \) increases at all process parameters and shows the tendency similar to that illustrated in Fig. 5: the rate of the maximum nanocone height increase is lower for the process of a higher ionization degree. An inset in this figure also illustrates the process in the time range of 0–500 s; in this case, one can notice that the curve corresponding to the higher ionization degree has a downward slope, i.e., the maximum nanocone height \( L_{\text{max}} \) decreases during the carbon deposition during the first 150 s into the process. In Fig. 7 we show the 3D visualization of the two carbon nanocone patterns grown in the process environments with ionization coefficients \( k_i=0.75 \) (a) and \( k_i=0 \) (b).

**IV. DISCUSSION**

Now we will discuss and interpret the results of the simulations of the carbon nanocone growth in the neutral gas- and plasma-based processes. We recall that our main aim here is to study the nanocone formation on Ni catalyst nanoparticle patterns, with the main focus on the nanocone height uniformity. The results will be discussed from the point of view of the two main processes: first, growth of nanocones by carbon influx through the catalyst (surface diffusion model), and second, carbon nanocone sputtering by the carbon ions (ion motion model).

One of the most important observations is that the distribution of the nanocone lengths is much narrower when the deposition process is conducted with the use of a carbon flux of a higher degree of ionization. Indeed, as is seen from Figs. 2–4, the width of the distribution \( \Delta_{W} \) obtained for the carbon flux with degree of ionization \( k_i=0.75 \) reaches 80 nm for the deposition time \( t_d=2500 \) s, but the deposition process with \( k_i=0 \) leads to a much wider distribution. For the case of a partially ionized carbon flux with \( k_i=0.25 \), the width reaches \( \Delta_{W}=250 \) nm. Another important observation is the nonzero minimum nanocone length \( L_{\text{min}} \) observed in the plasma-based process.

Thus, a conclusion can be made that the width of the nanocone distribution reduces strongly with an increase in the carbon flux ionization degree, and that this reduction is due to both the shortening of the nanocone maximum height \( L_{\text{max}} \) and increasing the minimum nanocone length \( L_{\text{min}} \), as illustrated in Figs. 2–6. The reasons for these two effects are different. It is quite clear that the reduction of the maximum nanocone height \( L_{\text{max}} \) is mainly due to the sputtering of the longest nanocones with energetic ions deflected by the strong electric field in the vicinity of the long nanocones, as has already been demonstrated by the numerical simulations.42 Besides, an effective use of the nanocone arrays as cold electron emitters proves the results of the electric field calculations.43 Thus we can conclude that the longest nanocones are effectively sputtered during the growth, and eventually the distribution function of the nanocone lengths is effectively restricted from the “long tail” side. On the other hand, an increase of the minimum nanocone length \( L_{\text{min}} \) cannot be explained by the direct influence of the energetic ions on the growing nanocones, since the smallest nanostructures (with the length of several tens of nm) create a much weaker electric field that is suppressed by the field of longer nanocones. To explain the increase in the minimum nanocone length \( L_{\text{min}} \), let us first examine the reasons of the occurrence of very short nanocones in the pattern.

We have already demonstrated in our previous works that the metal catalyst nanoparticles on the surface are saturated nonsimultaneously due to their different sizes; in the case of the plasma environment used, the redistribution of the electric field promotes more uniform (more simultaneous) saturation, i.e., reduction of the incubation time dispersion for the catalyst nanoparticles of different sizes.1,8,41 Nevertheless, with the nonuniform catalyst nanoparticles on the surface (note that the real technological processes of the metal nanopatterning usually result in the formation of metal island patterns with some size dispersion, see for example, Ref. 44), a completely simultaneous saturation cannot be achieved and thus the nanocones are nucleated at different time moments; as a result, some initial dispersion on the nanocone length is unavoidable. Then, the growth rates of the nanocones on metal catalyst nanoparticles depend mainly on the supply of carbon precursors from the surface to the nanoparticles. Since smaller nanoparticles have shorter perimeters, they collect lower fluxes of carbon species and eventually lead to lower nanocone growth rates; this effect also contributes to the nonuniformity of the nanocone lengths.

In the neutral gas and plasma-based processes, the nanocone pattern itself influences the growth of the shortest nanocones in different ways. In the neutral gas process, due to the random orientation of the velocities of neutral particles, most of the flux is collected by the long nanostructures and cannot reach the substrate.12 As a result, the shortest nanostructures (the nanocones in our case, but this conclusion may be related to any long nanostructures on the surface) are subjected to substantially lower carbon supply and eventually reach the zero-supply situation which results in the zero growth rate. Besides, some catalyst nanoparticles may get into the “zero-supply” conditions before they are fully saturated with carbon; as a result, these nanoparticles will be unable to nucleate nanocones and hence they will be “lost” for the array. Finally, in the gas-based process the zero-length tail of the nanocone length distribution is unavoidable. In the plasma process, the electric field created by the longest nanocones changes the ion flux distribution on the substrate, and spe-
cifically, provides deposition of the ions directly on the substrate surface between the nanostructures. Under such conditions the catalyst nanoparticles with the shortest nanocones on them collect (through the surface diffusion mechanism) a carbon flux sufficient to sustain the nanocone growth. As a result, the shortest nanocones grow and, most importantly, all the catalyst nanoparticles will be saturated and will not be lost for the array; thus, the array density will be the highest in this case.

Another effect that contributes to the increase in the minimum nanocone length $L_{\text{min}}$ is the redistribution of carbon atoms sputtered from the side surfaces of the longest nanocones. It is quite logical to assume that the sputtered carbon atoms sputtered from the side surfaces of the longest nanocones above that case, as can be seen from Fig. 4 that mean nanocone length $L_{\text{mean}}$ increases but the rate of the increase is lower for the process of a higher ionization degree. When $L_{\text{min}}$ is not too strong. In this case the nanocone array density will be the highest for the array; thus, the array density will be the highest in this case.

Thus, the observed results can be explained in terms of the three main effects, namely, the ion flux redistribution in the nanostructure-generated electric field, redistribution of sputtering-induced carbon flux, and preferential deposition of carbon atoms on the longest nanocones in neutral gas processes. Indeed, let us examine the behavior of the maximum nanocone height $L_{\text{max}}$ shown in Fig. 6. It was mentioned above that $L_{\text{max}}$ increases but the rate of the increase is lower for the process of a higher ionization degree. When $L_{\text{max}}$ is large enough, this can be explained by the intense sputtering of the longest nanocones. In the time interval of 0–500 s the maximum nanocone height for $k_e=0.75$ decreases. In this case, as can be seen from Fig. 4 that mean nanocone length $L_{\text{m}}$ is about 20 nm, and the maximum height $L_{\text{max}}$ is approximately 100 nm. Thus, at this stage the difference between $L_{\text{m}}$ and $L_{\text{min}}$ is not too strong. In this case the nanocone array creates a highly uniform electric field that effectively focuses an ion flux towards the substrate. As a result, carbon precursors are supplied uniformly to all growing nanocones (including the lowest ones). In other words, the longest nanocones no longer receive the largest fraction of the precursor flux; in addition, intense sputtering causes a significant shortening of the long nanocones.

V. CONCLUSION

In summary, we have demonstrated that the deposition parameters, and in particular, the degree of the carbon flux ionization, strongly affect the growth of carbon nanocone arrays on metal catalyst patterns. The use of the carbon flux with a very high degree of ionization (up to 75%) makes it possible to significantly narrow the nanocone length distribution. It was shown that the plasma-based process results in the nanocone arrays with a much shorter maximum length and without very short (shorter than 50% of the mean length) nanostructures. A competition of several effects, mainly redistribution of the ion flux and intense sputtering of the longest nanocones in the electric field, makes the plasma parameters effective controls to tailor the nanocone array properties and ultimately increase the array quality.

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