Reactive magnetron sputtering deposition and columnar growth of nc-TiC/a-C:H nanocomposite coatings

D. Galvan, a) Y. T. Pei, and J. Th. M. De Hosson

Department of Applied Physics, The Netherlands Institute for Metals Research and Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 4 May 2005; accepted 22 February 2006; published 23 June 2006)

TiC/a-C:H coatings were deposited using closed-field unbalanced reactive magnetron sputtering deposition from Ti targets. Different acetylene gas flow and substrate bias values were employed to vary the coatings' compositions and microstructures. The application of an external negative substrate bias increased the deposition rate of the plasma-enhanced chemical vapor deposition process from the reactive atmosphere. The sputtering of carbonaceous species from the poisoned targets surface was a minor source of C flux to the substrates. The application of an external substrate bias during deposition yielded films with a featureless cross-sectional structure, but the dominant parameter controlling the columnar growth was the chemical composition of the films. An explanation of this effect was formulated based on the microstructures observed and the deposition technique employed. © 2006 American Vacuum Society. [DOI: 10.1116/1.2188411]

I. INTRODUCTION

Diamondlike carbon (DLC) coatings represent an attractive solution to engineering problems where wear resistance and a low sliding friction coefficient are needed. The applications of these materials are particularly advantageous in high-load sliding contacts, where the low friction coefficient reduces the shear stresses exerted over the two counterparts. Furthermore, their mechanical properties can be easily varied over a wide range tailoring for the desired applications. The actual performance depends strongly on the hydrogen content and sp3/sp2 hybridization ratio.1 DLC coatings can be deposited using a variety of plasma processes, including magnetron sputtering deposition from graphite targets.2,3 Nevertheless, the use of a carbonaceous gas precursor such as acetylene (C2H2) is a more attractive approach as it yields higher deposition rates through a plasma-enhanced chemical vapor deposition (PECVD) process; this material is also known as hydrogenated amorphous carbon (a-C:H). During PECVD the gaseous precursor is activated in the plasma, with the generation of ionic or radical species that contribute to film growth. While certain studies indicate that radicals are the main species responsible for film growth, this will clearly depend on the particular deposition technique and processing parameters.4–6 Nevertheless, the film growth rate in PECVD processes generally varies as a function of the applied substrate bias, initially increasing due to enhanced plasma and surface activation and then decreasing due to resputtering and densification.7 The combination of magnetron sputtering and PECVD techniques in a hybrid process such as reactive closed-field unbalanced magnetron sputtering (reactive CFUBMS) is an attractive approach to DLC deposition. The presence of a magnetic field in the deposition chamber improves the ionization efficiency of the electrons in the plasma, permitting to run the process at low pressure. Furthermore, the use of a closed-field unbalanced configuration of the magnetrons can enhance the ion fluxes towards the substrates, along with increasing the ion bombardment.8 At the same time, the sputtered elements from the target can be introduced in the coating to dope the a-C:H matrix or to form transition metal (TM) carbides that can improve the material toughness and wear resistance.9 In this hybrid process the C flux to the substrate has contributions from both the magnetron sputtering of the poisoned target surface and PECVD of the reactive atmosphere.

In our research we used Ti targets and obtained nano composite coatings consisting of a distribution of TiC nanocrystalline (nc) particles in an amorphous hydrocarbon (a-C:H) matrix. The compositions, nanostructure, and mechanical and tribological properties of the coatings were thoroughly reported in our recent article,10 in which it was shown that the coatings with a columnar structure exhibit lower toughness. The deformation behavior after nanoindentation was studied through transmission electron microscopy (TEM) and focused ion beam (FIB).11 It was concluded that carbon-enriched columnar boundaries represent the weakest areas of the coatings. The formation of columnar structures should be avoided to maximize the coating toughness. The evolution of columnar microstructures of thin films can be interpreted in terms of structure zone models (SZMs),12,13 where commonly observed microstructural features are classified among different zones and depend on parameters such as deposition temperature, pressure, and ion bombardment. According to these models, the deposition of coatings at higher temperature, lower pressure, or higher intensity of ion bombardment reduces the columnar features and can result in coatings with a dense microstructure. However, the SZMs do not account for the influence of coating composition. The variation of the columnar structure of a-C films as a function of composition was studied in recent publications.14,15 It was observed that the gradual addition of transition metals decreased the columnar features of the coatings; the authors explained this...
effect in terms of crystallite-induced renucleation, i.e., a
gain refinement effect that improved the coating density and
smoothness. Our findings agree with literature for what con-
cerns the influence of the ion bombardment on the columnar
structure formation, whereas they strongly disagree for what
concerns the coating composition, for both H-free and hydro-
genated nanocomposite film depositions.2 Because of this
discrepancy in the results, it was decided to study in more
detail the growth mechanism of the coatings under our depo-
sition conditions. The influence of bias and relative flow of
acetylene on the atomic fluxes to the substrates was studied,
and the flux of sputtered Ti atoms to the growing interface
was modeled through a Monte Carlo simulation.

II. EXPERIMENT

A Hauzer HTC-1000 deposition chamber was used to de-
posit nc-TiC/a-C:H coatings by sputtering Ti targets in an
Ar/C2H2 reactive atmosphere. The detailed setup of the coat-
ing system has been documented elsewhere.16 The Ti metal
sputtering was performed from two targets opposite to each
other, while the other two available cathodes were mounted
with Cr targets that were used to introduce a graded inter-
layer between substrates and coatings; a detailed analysis of
the graded intermediate layer structure has been reported in
our recent article.17 The substrates were mounted on spindles
present on top of the substrate table; both the substrate table
and the spindles were rotated parallel to the vertical axis of
the chamber, generating a planetary motion of the substrates,
which were exposed periodically to the Ti targets during
deposition. Disks of hardened M2 steel, 304 stainless steel,
and Si wafers were mounted on the substrate holder and sputter cleaned in an Ar atmosphere. Subsequently, the
graded intermediate layer was deposited to improve adhesion
to the substrate. Towards the end of the intermediate layer
deposition, acetylene gas was introduced in the chamber to
initiate the reactive deposition of the nanocomposites. Coat-
ings were deposited at different negative substrate biases
(0–150 V) and in different Ar/C2H2 gas mixtures (26%–
36% relative flux acetylene). The gas flow of Ar was fixed at
225 sccm (sccm denotes cubic centimeter per minute at STP),
and the acetylene gas flow was varied between 80 and
125 sccm. The pumping speed during deposition was kept
constant, resulting in a working pressure of approximately
0.33 Pa, which did not vary as a function of the acetylene
gas flow in the range of 80–125 sccm. The targets were
sputtered at a constant applied power. No intentional sub-
strate heating was applied to the substrates during deposition,
and a rotating thermocouple was used to measure the tem-
perature rise during the process. Different deposition times
were used for the different deposition parameters to compen-
sate for varying growth rates. Coatings of thickness around
1.4 µm were obtained. The chemical composition of the
cOatings was measured through wavelength-dispersive elec-
tron probe microanalysis (WD-EPMA) with a Cameca
SX-50 spectrometer and the use of standards. An acceler-
a veloc voltage of 5 kV was employed to avoid excitation of X
rays from the interlayer area of the coating. A high-resolution
field emission scanning electron microscopy (SEM) (Philips
XL-30s) was used to measure the coating thickness. Low
acceleration voltage (3 kV) and small working distance
(3 mm) were employed to improve the obtained resolution,
and a special detector of the microscope was used in high-
resolution (HR) mode. Cross-sectional TEM samples were
prepared with a previously described method18 and these
were examined with a JEOL 2010F field emission gun (FEG)
microscope operating at 200 kV.

To gain an insight into the deposition process, a three-
dimensional Monte Carlo simulation of the Ti particle trans-
port in an Ar atmosphere was developed using the MATLAB
programming language. Analogous simulations gave very
promising results in predicting the deposition rate variation
over substrates or topological features.19,20 A proper simula-
tion of the process under our deposition conditions should
take into account the presence of reactive gas in the chamber
atmosphere together with Ar. Nevertheless, the partial pres-
sure of C2H2 during our depositions is expected to be very
low, as explained further in the text, and a simulation that
takes into account the reactive atmosphere would be signifi-
cantly more complex than the presently developed qualita-
tive model. Distributions of random numbers were generated
that followed the distributions of the physical parameters of
the sputtering process. The actual dimensions of the sputter-
ing chamber, targets, and racetrack were considered for the
simulation. Because of the complex geometry of the rota-
tional substrate holder, it was decided to monitor the sput-
tered particle flux that entered the cylinder delimiting the
substrate holder area. Ti atoms were emitted randomly from
locations corresponding to the racetrack over the target sur-
face. A Thompson distribution of the initial sputtered particle
energy was assumed,21 which takes into account the applied
target sputtering voltage and the binding energy of the target
material; a cutoff energy value was set at 30 eV for the en-
ergy distribution of the sputtered particles. A cosine law
of emission geometrical distribution of their initial traveling
direction was considered.22 Singular particles were emitted and
the trajectory of each particle was followed as it experienced
collisions with the working gas atoms. The particles with an
energy higher than the energy of the Ar working gas during
deposition (about 0.065 eV at 500 K) will be called “hyper-
thermal,” and the distribution of their mean free paths be-
tween collisions with Ar gas atoms was generated using an
energy-dependent cross section,21 while a hard sphere colli-
sion model23 was used to determine the direction and energy
of the particles after each collision. The particles of energy
below 0.065 eV, instead, will be called “thermalized,” and
they will follow a random Brownian-type motion. The path
of each particle terminates either when it enters the substrate
holder area or if it is backscattered to the target or if it hits the
chamber walls.

III. RESULTS

A. Deposition of TiC/a-C:H coatings

The coating processing parameters and compositions are
reported in Table I. The nanocomposite structure of the films
was analyzed in previous studies,\textsuperscript{24} where a procedure was developed to estimate the TiC volume fractions ($V_F$) in the films; the values obtained for a selection of coatings are also reported in Table I. The same assumptions used to calculate the TiC $V_F$ in the nanocomposite coatings are used in this article to compute approximate atomic fluxes to the substrates of the different species contributing to film growth as a function of the processing parameters. The computed atomic fluxes have the unit of at. s/cm\(^2\); and are absolute values for each different element (C, Ti, and O). Furthermore, from the ion current and the total area of the loaded substrate holder the ion current density over the substrate surface can be estimated that allows a computation of the neutral-to-ion flux ratios for each coating (ion number). Clearly this determination of the neutral and ion fluxes is only qualitative, but it can be useful when comparing different coatings.\textsuperscript{25} Indeed, the neutral species fluxes will be affected by an error due to the assumption of certain densities for the different phases and the description neglects resputtering effects due to ion bombardment. The estimate of the ion current density does not account for secondary electron emission from the substrate, the presence of multiply charged ions, or current inhomogeneity over the substrate holder surface. The average energy delivered per condensing atom parameter,\textsuperscript{26} $E_d$, is determined from the ion current, applied substrate bias, and growth rate assuming a collisionless plasma sheath.

By monitoring the deposition rates of the films it was realized that about 60\% of the acetylene introduced in the chamber is incorporated in the growing film, i.e., the reactive gas is gettered by the large surface of the substrate holder fixture, the percentage increasing slightly as the C\(_2\)H\(_2\) flux increases from 80 to 125 sccm. It is expected that a considerable portion of the reactive gas will also gettered by the metallic targets and the chamber walls. Therefore, following the expression proposed by Berg \textit{et al.},\textsuperscript{27} the partial pressure of C\(_2\)H\(_2\) in the chamber during deposition can be determined from the ratio of the flux of unreacted acetylene, which is low, and the pumping speed of the deposition rig, which is very high because of its large size. Indeed, an Ar flow of 225 sccm resulted in a pressure of 0.32 Pa in the chamber; the introduction of 80 sccm of reactive gas caused a modest increase of pressure, up to approximately 0.33 Pa, and no significant further increase of pressure was observed up to 125 sccm of acetylene. The introduction of acetylene into the chamber was accompanied by a progressive poisoning of the target. This was evident by monitoring the variation of target current as a function of acetylene gas flow. As 80 sccm of C\(_2\)H\(_2\) is introduced in the chamber, the target current decreases by about 8\%, and increasing the reactive gas flow up to 125 sccm causes an additional decrease of about 2\%. These figures suggest that, within the employed reactive gas flow range, the flux of C\(_2\)H\(_2\) does not have a major influence on the plasma characteristics, and also that during our depositions the Ti sputtering targets are not heavily poisoned. Nevertheless, it is expected that increasing the reactive gas flow results in an increasingly higher coverage of the target with a carbonaceous layer, that can eventually lead to the total poisoning of the target for C\(_2\)H\(_2\) flow rates above 125 sccm.

### B. Electron microscopy investigation of TiC/a-C:H coatings

The variation of coating morphology with deposition parameters is shown in Fig. 1. The coatings lose their columnar structure as the applied substrate bias or the relative acetylene to H\(_2\) partial pressure ratio increases from 100:125 (a) to 100:−100 (b). Figures (c) and (d) show cross-sectional micrographs of coatings deposited at constant substrate bias of −100 V (c) and −150 V (d), respectively, and relative acetylene partial pressures of 110:125 (c) and 80:125 (d). The coatings lose their columnar structure to form a nanocomposite with embedded carbon nanostructures. Figures (e) and (f) show cross-sectional micrographs of coatings deposited at different acetylene relative gas flow rates, constant substrate bias of −100 V, and different acetylene to H\(_2\) partial pressure ratios of 110:125 (e) and 80:125 (f). The coatings lose their columnar structure to form a nanocomposite with embedded carbon nanostructures.

### Table I. Deposition parameters, chemical composition, growth rates, and volume fractions of TiC nanoparticles of the coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Bias (V)</th>
<th>C(_2)H(_2) flow (sccm)</th>
<th>C (at. %)</th>
<th>Ti (at. %)</th>
<th>O (at. %)</th>
<th>Growth rate ($\mu$m/h)</th>
<th>TiC $V_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0V110</td>
<td>Float</td>
<td>110</td>
<td>71.3</td>
<td>13.6</td>
<td>15.0</td>
<td>0.71</td>
<td>3.2</td>
</tr>
<tr>
<td>60V110</td>
<td>−60</td>
<td>110</td>
<td>80.2</td>
<td>16.4</td>
<td>3.4</td>
<td>0.92</td>
<td>2.3</td>
</tr>
<tr>
<td>100V110</td>
<td>−100</td>
<td>110</td>
<td>81.0</td>
<td>17.8</td>
<td>1.1</td>
<td>0.88</td>
<td>2.2</td>
</tr>
<tr>
<td>150V110</td>
<td>−150</td>
<td>110</td>
<td>80.3</td>
<td>18.5</td>
<td>1.2</td>
<td>0.82</td>
<td>2.1</td>
</tr>
<tr>
<td>100V80</td>
<td>−100</td>
<td>80</td>
<td>66.6</td>
<td>31.7</td>
<td>1.6</td>
<td>0.67</td>
<td>3.7</td>
</tr>
<tr>
<td>100V125</td>
<td>−100</td>
<td>125</td>
<td>87.2</td>
<td>11.8</td>
<td>1.0</td>
<td>1.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\[ VF \] indicates the interface between the interlayer and film in each micrograph.
iene gas flow increases. TEM micrographs of the coatings deposited at a constant applied substrate bias of −100 V and different reactive gas flows are reported in Fig. 2. The coatings were observed at the locations where they start growing on top of the interlayer, visible in the bottom part of both pictures. Coating 100V80 has a pronounced columnar structure where C-enriched columnar boundaries delimit columns that show an inner branched structure. Coating 100V110 instead has a rather featureless structure where very thin and discontinuous columnar boundaries can be seen along the coating growth direction. No multilayered structure was observed in any area of the sample, which implies that the period of the compositional inhomogeneities deriving from the alternate exposure to the Ti targets is comparable to the ion-intermixing depth under the employed deposition conditions. Indeed, it was estimated that, for instance, in coating 100V110 an average growth of 1.2 nm followed each periodic exposure of each spindle to one of the Ti targets during deposition, and transport and range of ions in matter \(^{28}\) calculations indicate that a recoil depth of about 0.7 nm is expected for both Ti and C adatoms within a coating of this composition and density at the applied substrate bias value. It is therefore reasonable to expect a continuous and homogeneous intermixing of the elements to occur along the coating thickness.

C. Influence of deposition parameters on growth of TiC/a-C:H coatings

The variation of coating growth rate and atomic fluxes to the substrates as a function of the applied substrate bias for reactive depositions with a 32% relative acetylene gas flow (110 SCCM acetylene) is depicted in Fig. 3. The growth rate initially increases and then decreases slightly upon the application of an external substrate bias. The flux of O decreases rapidly as the substrate bias is increased. The flux of Ti increases slightly as a negative bias is applied and then remains approximately constant. The greatest flux variation is observed for C; its variation is analogous to the variation of growth rate, i.e., it goes through a maximum at −60 V bias. The variation of substrate bias also caused a variation of the ion current to the substrates, and therefore of the ionic flux. Plots of the variations of ion-to-neutral flux ratio, energy per atom deposited, and substrate temperature as a function of the applied substrate bias are reported in Fig. 3(b). The intensity and energy of ion bombardment clearly increase as a function of the substrate bias, which results in an increase of substrate temperature.

The variation of growth rate and relative atomic fluxes with the reactive gas flow is illustrated in Fig. 4(a). The growth rate increases together with the acetylene gas flow. It can be seen that the Ti flux decreases slowly with increasing reactive gas flow. This indicates that a gradual coverage of the target surface with carbonaceous phases occurs. Sputtering of Ti atoms from the target will be partially replaced by sputtering of adsorbed C species. The C flux instead increases with the acetylene gas flow. As the flow of reactive gas is increased, the ionization in the chamber remains approximately constant, as the current drawn to the substrates at constant applied bias decreases by less than 8%, while a significant increase of growth rate occurs, up to 54%. Consequently, a strong decrease of ion number and \(E_d\) occurs as the acetylene flux is increased, resulting in a less energetic deposition and a decrease of substrate temperature [see Fig. 4(b)].
D. Monte Carlo simulation of Ti particle transport during TiC/a-C:H deposition

The typical trajectories of 100 Ti particles after emission from the target racetrack in the Monte Carlo simulation are depicted in Fig. 5(a). It can be seen that a portion of particles reach the substrate holder area, while others are backscattered or hit the chamber walls. The results of the simulation for $5 \times 10^6$ particles indicate that at this operating pressure, 58% of the emitted particles are able to enter the substrate holder area, 53% of which are hyperthermal and 47% are thermalized. 26% of the particles are backscattered to the target, while 16% of them are lost to the chamber walls. For the particles entering the substrate holder area a broad distribution of energy was observed, with an average value of 3.2 eV. Most hyperthermal particles experience one collision before entering the substrate holder area, while the average value is 2.2. The thermalized particles undergo significantly higher number of collisions because of their shorter mean free path and random motion. The final distribution of the deposited Ti flux over the surface delimiting the substrate holder area is shown in Fig. 5(b). The flux of Ti atoms is rather diffuse, but it seems to concentrate slightly in front of the center of the sputtering target. The particles enter the substrate holder area with a broad angular distribution, and their average angle of incidence is about 40°, which implies that according to the model, the Ti atoms approach the substrate holder area at oblique angles. Considering that the substrates undergo a planetary motion within this area during deposition, it can be concluded that the Ti particle flux approaches the substrates with a random distribution of directions, which will favor shadowing effects during growth.

IV. DISCUSSION

In the hybrid process of magnetron-enhanced PECVD of acetylene an additional contribution to the C flux to the substrates is expected from the magnetron sputtering of the carbonaceous layer poisoning the target surface. Nevertheless, the observed trends for the C flux and growth rate curves as

Fig. 4. Deposition characteristics as a function of the relative acetylene gas flow for coatings 100V80, 100V110, and 100V125. (a) Variation of growth rate and atomic fluxes of O, Ti, and C. (b) Variation of $E_D$, neutral/ion flux (ion number), and substrate temperature.

Fig. 5. (a) Top view of the deposition chamber and typical trajectories of 100 particles during the Monte Carlo simulation; they are emitted from the target at the bottom of the figure and can reach the substrate holder area, modeled as a cylinder. (b) Distribution of particle flux over the cylinder surrounding the substrate holder area along the whole chamber height. The abscissa is the position of the flux along the circumference of the cylinder. The color bar indicates the number of particles per pixel for a simulation with $5 \times 10^6$ particles.
a function of bias are typical of PECVD of a-C:H from Ar/C_2H_2 atmosphere, i.e., it goes through a maximum with increasing substrate bias. This is compatible with a minor contribution to the flux from the C poisoned layer for our processing conditions. Indeed, this contribution would not be enhanced by the substrate bias. The decrease of growth rate at higher substrate bias levels can be due to resputtering, but also to densification of the films, as the growth rate was estimated only from the thickness of the films rather than their density. Our results indicate that resputtering is already active at low bias levels, but mainly on the removal of oxygen atoms, which is a typical feature for magnetron-sputtered coatings. At higher substrate bias levels the analysis indicates that C is preferentially resputtered with respect to Ti, decreasing the C/Ti ratio. The analysis of the elemental fluxes as a function of acetylene gas flow indicates a modest decrease of Ti flux as the target poisoning progresses, which confirms that the PECVD process is the dominant source of C flux to the film.

A substantial decrease of columnar features was observed with increasing applied substrate bias at constant flow of acetylene, i.e., the columns observed in the cross-sectional SEM micrographs become less and less separated as the substrate bias is increased, finally resulting in a featureless structure in coating 150V110. This variation of columnar features is expected as a result of the increase of ion bombardment and substrate temperature during deposition. On the other hand, the evolution of columnar structure as a function of the gas flow is not what one would expect. In fact, in this case the variation of ion number, the energy deposited per atom, and the substrate temperature would not favor the disruption of columnar features at higher acetylene flux. Indeed, most columnar films were obtained at the highest values of ion number, $E_d$, and substrate temperature. By no means does this implies that these parameters influence the growth of the films in the opposite way than generally expected; instead, it is an indication that they do not influence the microstructural evolution as much as parameters related to the film composition do. It is expected that if the ion number, $E_d$, or substrate temperature was increased for the columnar films, these would naturally tend to have a more featureless cross-sectional structure. In fact, no voids were observed within the columnar boundaries of the coatings obtained at low acetylene flow rates, which is a consequence of the energetic deposition. Instead, these were C enriched, and the column bodies showed a branched structure where the individual branches are separated by C-enriched areas. It seems that the progressive introduction of metal is the cause of the columnar structure formation, which does not agree with the results of Nilsson et al.\textsuperscript{14,15} The reason for such a strong tendency of Ti-rich layers to have a columnar microstructure is difficult to identify. Several factors can be pointed out based on different properties of Ti and C-growth-contributing fluxes. The influences of temperature, pressure, and ion bombardment in the SZMs are based on modifications of adatom mobilities, shadowing effects, and resputtering effects, respectively. In the following various mechanisms are proposed by which the compositional variation would modify these parameters in the same way as the parameters generally considered in SZMs do.

**Adatom mobility.** The introduction of Ti atoms leads to the formation of TiC particles, whose presence on the growing interface is likely to modify the adatom mobility. Indeed, at lower acetylene fluxes the Ti concentration is higher, and a larger fraction of the film interface will be covered by TiC islands, which in turn can also enhance shadowing effects.

**Shadowing.** It is shown with the Monte Carlo simulation that the Ti flux emitted from the target will deposit on the substrates with a diffuse angular distribution, favoring shadowing effects. The C flux would be directional in the case hydrocarbon ions were the main growth-contributing species, but diffuse in the case the growth was mainly based on radicals. Unfortunately the relative contributions of ions and radicals to film growth could not be identified within the present work.

**Resputtering.** It is shown that C atoms are preferentially resputtered with respect to Ti during deposition. This represents an important difference of property between the Ti and C-growth-contributing fluxes. Furthermore, C atoms are lighter than the incident Ar ions, whereas Ti atoms are heavier. For this reason C is more likely to be knocked down to fill voids and reach shadowed portions of the coating following bias-induced ion bombardment, promoting structural rearrangement.

A final observation is that the microstructure observed in the TEM micrograph of Fig. 2(a) has a striking resemblance to what is observed in generalized growth models\textsuperscript{29} such as ballistic or diffusion limited aggregation (DLA), where particles reach the growing interface perpendicularly or randomly, respectively, and stick where they hit the surface. On the other hand, models that take into account surface relaxation mechanisms predict homogeneous structures such as the one depicted in Fig. 2(b). Nevertheless, the microstructure shown in Fig. 2(a) was obtained at a higher ion number than the microstructure shown in Fig. 2(b). This observation would suggest that the relative surface mobility of Ti and C atoms is the most important parameter governing the columnar growth of these nanostructured coatings.

**V. CONCLUSIONS**

The deposition of nanocomposite nc-TiC/a-C:H coatings through CFUBMS reactive deposition under the presently employed deposition conditions relies predominantly on the PECVD process for the deposition of C, and on magnetron sputtering of the metallic target for the introduction of Ti. The evolution of columnar structures in the coatings with substrate bias follows the general behavior expected from SZMs for the growth of thin films. When the Ti concentration is decreased by enhancing the PECVD process, instead, the ion number, $E_d$, and the substrate temperature decrease, while the structure becomes less columnar. By considering only the energy parameters as generally considered in SZMs this would not be expected. Various mechanisms are proposed by which the compositional variation can influence the
film growth mode in the same way as temperature, pressure, and ion bombardment influence growth in conventional SZMs.

ACKNOWLEDGMENTS

Christian Strondl from Hauzer Technocoating BV (Venlo, NL) is gratefully acknowledged for his help in the deposition of the coatings. Albano Cavaleiro of the University of Coimbra, Portugal is gratefully acknowledged for the EPMA measurements. The authors acknowledge financial support from the Netherlands Institute for Metals Research (NIMR) and the Foundation for Fundamental Research on Matter (FOM-Utrecht).

28www.srim.org