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Variable roughness development in statically deposited SiO₂ thin films: a spatially resolved surface morphology analysis

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Abstract
For the first time a systematic analysis of the growth front evolution of statically deposited silica films in an atmospheric pressure-plasma enhanced chemical vapour deposition (AP-PECVD) reactor was carried out. The growth front evolution was studied as a function of time and position in the reactor. Focussed beam spectroscopic ellipsometry was used to assess the local film growth rate and atomic force microscopy (AFM) to analyse the surface roughness development. Spatially resolved AFM analysis showed a strong dependence of the rms roughness on the position, and consequently on the thickness and local deposition rate (LDR), in the reactor. Time resolved surface morphology analysis at two specific positions at high and low LDR indicated different growth exponents $\beta = 0.33$ and $\beta = 0.11$, respectively. From the analysis of the static roughness development in the AP-PECVD reactor certain limitations on the deposition time and the maximum LDR for dynamic or web rolled deposition conditions have been elucidated. Moreover, the system is characterized by a set of roughness exponents $\alpha_{loc} = 0.9$, $\alpha_s = 1.6$ and global roughness exponent $\alpha = 2.3$. The different values of $\alpha$ indicate an anomalous scaling behaviour of the system whereas different growth exponents $\beta$ suggest a breakdown of the anti-shadowing mechanism.

Keywords: atmospheric pressure PECVD, silicon dioxide thin films, atomic force microscopy, anomalous scaling

(Some figures may appear in colour only in the online journal)

1. Introduction

High performance moisture barrier films deposited on polymer substrates are required for encapsulating flexible OLED, photovoltaic devices and quantum dot displays in order to achieve the desired device lifespan [1]. A defect free and smooth surface is considered to be a key factor in achieving excellent performance of the moisture barrier coatings for flexible electronics [2–4]. Understanding the growth mechanism and the surface structure at the nanometre length scale is therefore of paramount importance to control the surface roughness and to precisely predict the functional properties of the thin film [5–8].
Recently it was demonstrated that high quality dense inorganic films can be synthesized on polymers from roll-to-roll utilizing an atmospheric pressure plasma enhanced chemical vapour deposition (AP-PECVD) process [9, 10]. Silica-like moisture barriers on PEN foil with a WVTR <6 · 10^{-6} g · m^{-2} · d^{-1} were successfully achieved. Premkumar et al [11] reported ultra-smooth SiO2 layers grown in a flat parallel plate AP-PECVD reactor operating in a high current dielectric barrier discharge. The films were grown in a self-similar way having unique scaling characteristics of time invariant surface roughness growth [11, 12] up to thickness values of 350 nm.

Generally the flux of fragments during the deposition process is assumed to be uniform and constant in time for PECVD reactors requiring a uniform discharge. However, due to a strong precursor depletion in the reactor, the deposition rate profile along the gas flow is highly non-uniform [13, 14]. As a result, a variable local deposition rate (LDR) exists which is controlled by the local precursor partial pressure and the flux of precursor fragments arriving at the surface. In the recent studies [13, 15] using spatially resolved ATR-FTIR analysis it was demonstrated that the film microstructure is significantly affected by the gas residence time and LDR (local vapour pressure of the organosilicon precursor).

Attempts to model the time invariant film growth observed in AP-PECVD were unsuccessful both for the continuum and discrete surface growth models. However, in a recent study by Merkh et al [16] the conventional Monte Carlo simulation was adjusted for the high pressure regime in which the mean free path of the depositing particles is considered to be on the same order as the surface feature size. More specifically, in the Monte Carlo simulation [16], the short mean free path of the depositing species results in a mean collision height above the surface. Hence, the actual particle trajectory towards the surface can result in a time invariant roughness evolution. Such an anti-shadowing mechanism can explain the time invariant roughness evolution in dynamically deposited films as previously reported in the work of Premkumar et al [11, 12].

Prior studies on the surface roughness evolution were mainly carried out in vacuum batch reactors and at AP under dynamic deposition conditions (showing a time invariant roughness development). In the latter case the potential roughness development due to variations in the LDR cannot be unravelled and this variation is inherently integrated into the film growth history [11, 12]. Thus, we take a step back to study the locally resolved surface dynamic evolution in a PECVD reactor operating at AP i.e. taking into account the growth stages that evolve under different LDRs without transportation of the substrate.

In this study we show that the surface roughness evolution is not locally invariant in the reactor. The film growth mechanism under AP is much more complex and to obtain a better understanding of the growth process the variable deposition rate should be accounted for. A further aim is to contribute to the development of a new elaborated growth model for PECVD at AP in the context of an industrially relevant cylindric roller-to-roll geometry under process conditions used for barrier deposition. In addition, the understanding of the growth dynamics under static deposition conditions can be exploited to achieve smooth and defect free films grown under dynamic, or web rolled, deposition conditions.

2. Experimental section

The SiO2 coatings were deposited in a roll-to-roll AP-PECVD reactor with a parallel bi-axial cylindrical electrode geometry described in detail elsewhere [9, 13]. The reactor itself is enclosed in an ISO class 3 cleanroom, in accordance with ISO 14644-1 standards to prevent contamination of the substrate surface by airborne particles. The process gas effluent is removed from the process in a general exhaust. Both electrodes were covered with a polymeric foil, on the top electrode AGFA PET and on the bottom electrode Polyethylene-2,6-naphthalat (PEN) foil which also provided the substrate for deposition. The copper electrodes were heated to 80 °C ± 1 °C by means of spiral oil-filled tubes located on the inner surface of the metal electrode casing. In the previous study the control of the substrate temperature during the discharge was evaluated [9]. There it was concluded that an surface temperature increase during the discharge is typically 40 °C–50 °C above the temperature of the circulating oil which does not significantly change in time along the discharge zone.

In this study the static thickness profiles were synthesised on the bottom electrode which was kept fixed while the top electrode moved with a constant speed of 50 mm · min^{-1}. The applied voltage between the electrodes was 2–3 kV and the frequency ranged from 180–200 kHz. The dissipated power in the discharge was 575 W corresponding to approximately 19.2 W · cm^{-2} specific power density with characteristic discharge expansion length of around 2 cm. The discharge width was 15 cm and the smallest gaseous gap was 0.5 mm. Silica like forming monomer was Tetraethoxysilane (TEOS) and the process gasses were nitrogen and oxygen. Nitrogen gas was used as a carrier gas with a flow rate of 18 slm. TEOS was diluted with 1 slm argon, and the reactant gas flows were kept constant at 1.8 · 10^{-3} slm TEOS and 0.5 slm oxygen. For the present experimental arrangement approximately 70% of the supplied gas flow was contributing to the deposition process. The gas loss can be attributed to intentional ‘leaks’ such as the narrow gap (≈100 μm) between gas injector and the cylindrical electrodes. All the reactant gases were mixed in the buffer chamber before they were introduced into the plasma. For the studied conditions the reactor was operating in the complete precursor depletion mode [9].

The static films were deposited on a buffer layer to prevent undesirable interaction of non-depositing species with the polymer [13, 17]. The protective silica (buffer) layer was deposited at a precursor flow of 8.2 · 10^{-3} slm and a web speed of 1 m · min^{-1}, which resulted in a thin SiO2 layer of 20 nm. The duration of the static depositions was varied in the range of 10–90 s.

The variation of the film thickness profile and deposition rate along the gas flow was characterized by means of focused beam spectroscopic ellipsometry with a spot size of 120 μm (M-2000D, J.A. Woollam Inc.). The spectroscopic ellipsometer was equipped with an automated translation table with a step size of 100 μm which allowed space
resolved measurements over the deposition width. To correct positioning errors, the peak maximum of the profiles is determined by taking the derivative of the thickness profile and subsequently re-aligning the profiles according to the value of the maximum thickness. These positioning errors (Δx) can be introduced during the deposition process as well as the thickness measurement, and are estimated to be Δx = ±0.5 nm.

The surface morphology of silica-like films was measured using atomic force microscopy (AFM) (Park Systems NX10) in non-contact mode with a tip radius of about 8 nm. In order to investigate film morphology evolution, AFM images of 512 × 512 pixels were obtained with scanning areas of 2 × 2 μm². The surface morphology of each experimental point was measured at least three times to improve the statistics and to obtain representatives images. It should be noted that all the samples are deposited on the buffer layer. The buffer layer is characterized by the root mean square (rms) roughness of 1.36 ± 0.04 nm which is smoother than the surface roughness of bare PEN (∼1.75 nm). The rms roughness of the individual profile of 90s deposition time was measured as a scan through the deposition width of the sample. The probe tip was changed as needed to maintain good quality of images. After the tilt corrections, the roughness of the films is calculated as the rms of the surface heights at different surface points. AFM images were analysed using open source Gwyddion software [18].

2.1. Method of data analysis

The surface height profile, obtained from AFM, can be characterised by the rms roughness or also known as the interface width (w). This well-known entity provides a measure for the overall roughness of the surface. Family and Vicsek [19] introduced dynamic scaling to describe both the temporal and spatial scaling behaviour. The growth mechanisms can be understood by analysing the surface morphology within the framework of the dynamic scaling theory (DST) characterized by the roughness (α), growth (β) and dynamic (z) exponents. In the framework of the DST it is possible to set up relations between pairs of α and β exponents and it’s ratio z = α/β to identify the type of growth mode. Thus, depending on the different surface relaxation mechanisms such as surface diffusion, shadowing, etching, etc. a particular set of scaling exponents is obtained. This concept proved to work in explaining the growth mechanism for various techniques such as sputtering, CVD and PECVD [20–23]. The roughness is calculated as the rms of the measured surface heights which is defined as:

\[ w(t) = \sqrt{\langle [h(r, t) - \langle h \rangle]^2 \rangle}, \]  

where \( h(r, t) \) is the height of the surface at a position \( r \) and time \( t \), and \( \langle h \rangle \) is the mean height of the surface. The interface width describes the correlation with growth time according to \( w(t) \sim t^\beta \). The rms roughness value describes only the vertical properties of a surface. Therefore correlation functions must be introduced such as the height–height correlation function (HHCF) which is defined as:

\[ H(r, t) = \left\langle [h(x + r, t) - h(x, t)]^2 \right\rangle, \]  

where \( h(x, t) \) represents the surface height at position \( x \) on the scanned area. The power spectral density function (PSDF) which is defined as:

\[ P(k, t) = \langle H(k, t) H(-k, t) \rangle, \]

where \( H(k, t) \) is the Fourier transform of the surface height in a system of lateral size \( L \) and \( k \) the spatial frequency in the reciprocal space [24].

Another scaling framework is the anomalous scaling where a local (αloc), spectral (αs) and global (α) roughness exponent \( \alpha_{loc} \neq \alpha_s \neq \alpha \) are introduced to describe the surface growth of the films [25, 26].

The anomalous scaling approach leads to the following scaling relations of the HHCF:

\[ H(r, t) \sim \begin{cases} \mu(t)^{2\alpha_{loc}}, & r \ll \xi(t) \\ (2r^2(t))^{\alpha_s}, & r \gg \xi(t) \end{cases}, \]

where \( \xi(t) \) is the lateral correlation length defined as the largest distance in which the height is still correlated and, \( \alpha_{loc} \) is the local roughness exponent. The time-dependent behaviour of the lateral correlation length is often found to be a power-law \( \xi(t) \sim t^{\alpha_s} \), where \( z \) is the dynamic exponent [19, 24, 27]. The local slope of the surface profile is denoted by \( m \).

In the anomalous scaling the interface width takes the following scaling form,

\[ w(t) \sim \begin{cases} t^\beta, & t \ll \tau \\mu_{loc} \\ \tau_{\mu_{loc}}^{\alpha_s}, & t \gg \tau \end{cases}, \]

where \( t \) is time, \( \kappa = \beta - \alpha_{loc} z \) (anomaly factor) and \( \alpha_{loc} \neq \alpha \). Such behaviour is observed when the local slope, \( m \), evolves with a power law in time as \( m(t) \sim t^{\kappa} \) [27].

The PSDF can be expressed in the following scaling form,

\[ P(k, t) = k^{-(2\alpha_s+1)} \left( k^\frac{1}{z} \right), \]

where the spectral roughness exponent \( \alpha_s \) is a new and independent exponent [25].

The relationships between these three roughness exponents and the scaling class they belong to can be summarized as follows [25]:

\[ \begin{cases} \text{if } \alpha_s < 1 \rightarrow \alpha_{loc} = \alpha_s \rightarrow \text{Family–Vicsek} \\ \alpha_s \neq \alpha_{loc} \rightarrow \text{Intrinsic anomalous} \\ \text{if } \alpha_s > 1 \rightarrow \alpha_{loc} = 1 \rightarrow \alpha_s \neq \alpha \rightarrow \text{Super–rough} \\
\end{cases} \]

\[ \begin{cases} \text{Family–Vicsek} \\ \text{Intrinsic anomalous} \\ \text{Super–rough} \\
\end{cases} \]

3. Results and discussion

3.1. Characterisation of the substrate morphology and static profiles

The precursor depletion along the gas flow within the discharge length of the DBD reactor results in a highly
non-uniform film thickness, and the LDR profile, as reported in [13]. Figure 1(a) shows the thickness profiles as a function of the position, $x$, in the reactor for different deposition times between 10–90 s.

In all the thickness profiles of figure 1(a), one can clearly observe two peak values, the first peak starts immediately at the discharge entrance at $x = -7$ mm and the second peak with the highest deposition rate at $x = -4.3$ mm. Both peaks are observed at the same relative position independently of deposition time. After the second peak the thickness rapidly decreases due to the depletion of the precursor. The zero position on the $x$ axis of the thickness profile corresponds to the smallest gap distance between the cylindrical electrodes. In an earlier study [13] the presence of two maxima was attributed to a difference in the transport kinetics of the precursor fragments arriving to the surface. It was suggested that the fragmentation degree and density of the precursor molecules change in a very short time scale, causing non-uniformity in thickness and also in the microstructure in the gas flow direction. The time dependent deposition profiles variation of the 10s profile suggests that the first peak may be caused by transient effects.

From the integrated values of the static profiles the film thickness can be obtained if the films are grown dynamically for different residence times, see figure 1(b). The integrated film thickness is linearly increasing with the deposition time and from the slope of the line an average deposition rate of 5.4 nm · s$^{-1}$ is obtained.

3.2. Spatially resolved analysis of the surface morphology

To understand whether the variations in the thickness play a role in the surface morphology evolution a comprehensive
space resolved analysis is performed on the sample deposited at $t = 90$ s. Figure 2 shows the dependence of the rms roughness on the position in the profile and correlates the rms roughness to the local film thickness. A strong correlation between the thickness and the rms roughness of the static deposition profile is observed. In the region of $x < -2$ mm, with a high precursor partial pressure, a clear roughness increase is observed, whereas in the precursor depleted region with $x \geq 0$ mm the roughness development is small.

The semi-log plot of figure 2(b) indicates an exponential dependence of the rms roughness with the local film thickness ($d$), or local flux of depositing species. Fitting the data according to an exponential relation, with $\text{rms} \sim \exp(d/d_c)$, yields a critical film thickness $d_c = 650$ nm. So, for a deposition time of $t = 90$ s and $d > d_c$, the surface roughness significantly increases whereas well below 650 nm the layer remains rather smooth, see figure 2(b).

Based on the critical film thickness, a critical deposition rate can also be defined, as the roughness will develop over time. Such a critical deposition rate can be used to set a limit to the maximum allowable LDR for which smooth films can be obtained. For the present deposition condition the critical LDR is $\sim 7.2$ nm $\cdot$ s$^{-1}$. By increasing the carrier gas flow to 30 slm, the convective transport of depositing species is increased and the maximum LDR is reduced [15]. Consequently, the roughness is much less and a relatively smooth surface is obtained over the entire static deposition profile, see figure 3.

3.3. Time dependent film front growth analysis for high and low LDR

To examine the evolution of the surface morphology in time, two specific regions in the thickness profiles of figure 1 were analysed, one region above and one region below the critical film thickness. More specific, at the maximum deposition rate which corresponds to a LDR $= 10.7 \pm 0.6$ nm $\cdot$ s$^{-1}$ at the position $x = -4.3 \pm 0.5$ mm and at the centre position at $x = 0 \pm 0.5$ mm with a LDR $= 5.4 \pm 0.6$ nm $\cdot$ s$^{-1}$. Typical examples of the evolution in time of the morphology of the SiO$_2$ film are shown in the $2 \times 2 \mu$m$^2$ AFM images of figure 4.

The morphology of the surface exhibits a grain-like structure for $t > 10$ s, in particular for the high LDR position. In figure 5, a typical cross-section of the AFM images of figure 4 is shown. Both lateral and vertical dimensions of the surface features increase with deposition time, and the grain growth for the high growth rate is more pronounced than for the features at low growth rate. The feature size increases from 30 nm up to 150 nm with the deposition time from 10 s to 90 s at the position of the maximum LDR.

The variation of the surface roughness with deposition time is illustrated in figure 6. The growth exponent $\beta$ is determined from the plot of the roughness versus deposition time in a double-logarithmic scale. Then, a linear regression is applied to obtain the slope which yields the value of $\beta$. At LDR $= 10.7$ nm $\cdot$ s$^{-1}$ the growth exponent $\beta = 0.33 \pm 0.05$, and at LDR $= 5.4$ nm $\cdot$ s$^{-1}$ a $\beta = 0.11 \pm 0.02$ is obtained. It should be noted that for $x > 0$ mm the growth exponent $\beta$ is even further decreasing ($\beta < 0.11$), and at $x = 8$ mm and $t = 90$ s the rms roughness is 1.8 nm, see figure 2(a).

Previously observed time invariant film growth front in the dynamically deposited films, which was attributed to anti-shadowing [16], may thus be overruled in the statically deposited films when the flux of fragments to the surface becomes too high.

On the other hand when the flux of fragments to the surface is relatively low, the anti-shadowing mechanism starts to play
a role which leads to time invariant film growth in this region of the static profiles.

Apparently the growth exponent $\beta$ depends on the flux of fragments which is relevant for understanding the growth dynamics of the films when the substrates are transported through the discharge and undergo these multiple growth stages. If a single growth mechanism for SiO$_2$ would exist in AP-PECVD, only a single value of the growth exponent, independent of processing parameters, should be observed in the system. The failure in describing the surface morphology with only one growth exponent was observed by many authors [20, 28–31] and usually indicated the existence of cross-over effects or multiple growth regimes but it was never reported to be an inherent feature of the deposition process.

To understand the time invariant film roughness in the dynamic deposition process it should be realised that the roughness increase at all positions in the reactor remains small for relatively short processing times ($t < 10$ s), as pursued in the dynamic deposition process in the previous studies [11, 12]. This indicates that a much longer deposition time is required to obtain a notable roughness increase in the dynamically deposited films. If the flux of precursor fragments is high and the deposition time is long ($t \gg 10$ s) then the surface roughening of the film is inevitable under dynamic deposition conditions.

3.4. Second order statistics

Because the global roughness of the films is determined from the rms roughness, it does not reflect the short range roughness. A measure of the short range roughness can be deduced from the roughness exponent $\alpha$. This quantitative information of the surface morphology can be extracted from different correlation functions. In this work two functions are employed to derive the roughness exponents $\alpha_{loc}$ and $\alpha_s$ from: (i) the HHCF defined as in equation (4); (ii) the PSDF defined as in equation (6). In figure 7 the HHCF for high and low LDR of SiO$_2$ films for $t = 10$ to 90 s are shown. The value of $\alpha_{loc}$ is calculated from the slope of the initial linear part of the HHCF curves using the exponential correlation model for isotropic self-affine film growth [32].

The calculated roughness exponent $\alpha_{loc}$ increases with the deposition time for both the high LDR and low LDR and then saturates at 30 s deposition time at a value of around $\alpha_{loc} = 0.99–1.0$. In addition, for small values of $\tau$ (less than the correlation length) the curves of the HHCF do not overlap, except for the 10 s deposition profile. For high LDR the local slope, $m$, gradually increases which implies that the film growth is nonstationary, and this behaviour is not in agreement with the requirements of the conventional DST. The nonstationary behaviour of the HHCF suggests an anomalous scaling which is commonly observed for films prepared by PECVD [26]. Note, that for the low LDR the local slope is not increasing.

To clarify the anomalous growth behaviour the spectral roughness exponent ($\alpha_s$) is calculated from the PSDF. Here, $\alpha_s$ is calculated from the slope $i$ of the linear region of the PSD functions as $\alpha_s = (i - d)/2$ where $d = 1$ for the one-dimensional PSD functions. In figure 8, the PSDF of the SiO$_2$ films for $t = 10$ to 90 s in log–log scale for the high and low LDR position are shown. One can notice the existence of two slopes in the PSDF. This subtle transition occurs at the same spatial frequency and the corresponding surface feature size can be estimated $L_C \approx 30$ nm. Interestingly this is the size of the smallest granular feature existing in both the high and low LDR region. While at high
The feature size continues to grow with deposition time for low LDR the granules enlarge only slightly. The values of the local and spectral roughness exponents are plotted in figure 9. Typical values for $\alpha_s$ obtained from the linear region of the high $k (>0.08 \text{ nm}^{-1})$ part of the PSDF are around 1.6. Meaning that the system shows an anomalous scaling behaviour as $\alpha_s \neq \alpha_{loc}$ which indicates that a new exponent enters the scaling, with $\alpha_s > 1$ and $\alpha_{loc} \sim 1$.

Figure 7. HHCF as a function of the distance $r$ is plotted in log–log scale. The curves correspond to deposition time from 10 to 90 s in (a) high LDR at $x = -4.3\text{ mm}$; (b) low LDR at $x = 0\text{ mm}$.

Figure 8. PSDF is plotted in log–log scale, the curves correspond to a deposition time of 10 up to 90 s in (a) high LDR at $x = -4.3\text{ mm}$; (b) low LDR at $x = 0\text{ mm}$.

Figure 9. Roughness exponent determined for local roughness exponent (black squares) and global roughness exponent (red squares): (a) high LDR; (b) low LDR, as a function of time.

LDR the feature size continues to grow with deposition time for low LDR the granules enlarge only slightly.

The values of the local and spectral roughness exponents are plotted in figure 9. Typical values for $\alpha_s$ obtained from the linear region of the high $k (>0.08 \text{ nm}^{-1})$ part of the PSDF are around 1.6. Meaning that the system shows an anomalous scaling behaviour as $\alpha_s \neq \alpha_{loc}$ which indicates that a new exponent enters the scaling, with $\alpha_s > 1$ and $\alpha_{loc} \sim 1$.

Figure 10(a) shows the increase of the lateral correlation length as a function of the deposition time. Applying the scaling relation $\xi(t) \sim t^{1/z}$ yields the dynamic exponent, $z$, as determined from the slope of the log–log plot. Dynamic exponents of $z = 6.6 \pm 1.8$ and $z = 16.6 \pm 5.5$ are obtained for the positions $x = -4.3\text{ mm}$ and $x = 0\text{ mm}$, respectively.

Sinha et al [32] proposed the following analytical form of the HHCF for an isotropic self-affine surface:
With this exponential model the local slope equals to
\[ m = \frac{\sqrt{2}w}{\xi \alpha} \]  

From the relation between \( \alpha = \kappa \cdot z + \alpha_{loc} \), the global roughness exponent can be determined from the dynamic exponent \( \kappa \). The global roughness exponents for high LDR is obtained from the relation \( \alpha = \kappa \cdot z + \alpha_{loc} \) which results in \( \alpha = 2.3 \pm 0.3 \). In table 1 the different scaling parameters are listed as obtained from the static profile analysis.

The variation of the roughness exponents \( \alpha_{i} \neq \alpha_{loc} \neq \alpha \) and the growth exponent \( \beta \) varying with the LDR suggests that the system belongs to a new anomalous scaling class [25]. However, not all systems can be assigned to one of the universal classes. In general, the scaling exponents deduced from these analyses are correlated to the theoretical predictions, and the mechanisms controlling the growth of the film can be understood. Even though the exact mechanisms has not been understood yet, similar exponents were obtained by Yanguas-Gil et al [34]. They showed that the anomalous scaling behaviour can be reproduced, by a kinetic Monte Carlo simulation of the growth of SiO\(_2\), SiO\(_2\) thin films prepared by PECVD [34, 35]. In the model by varying angular distribution function of the incoming particles, a wide range of growth exponents was obtained [34]. The main factor responsible for anomalous scaling of the growth process was attributed to lateral grain growth due to nonlocal effects of shadowing [35, 36]. The films depicted a well-defined granular microstructure and were characterized by values of \( \alpha_{i} = 1.3 \) determined in the PSDF, and values of \( \alpha_{loc} = 0.7 \) obtained from the HHCF [34, 35]. A recent experimental study [37] on the surface evolution of CdS thin films grown by the chemical bath deposition technique resulted in a similar set of scaling exponents of \( \alpha = 2.2, \alpha_{i} = 1.49 \) and \( \alpha_{loc} = 0.78 \). Nevertheless, in this study at AP the system presents an anomalous scaling behaviour although the process is not characterized by a high growth exponent as observed by others [33, 34, 37, 38]. Even though the LDR is varied within the discharge region the fact that the local and spectral roughness exponents are not affected by the LDR may suggest a uniform activation of the precursor within the discharge.

In contrast to the growth history of the statically deposited films having an intrinsically local roughness development with \( \beta \neq 0 \) is in the dynamically deposited films a time invariant roughness growth is observed, which was explained by the anti-shadowing mechanism [16]. The formation of seed protrusions is proposed as a mechanism triggering the surface roughness increase which depends on the flux of depositing species. From the static profiles it can be concluded that the anti-shadowing mechanism is mainly dominating the film growth at a relatively low flux of depositing species. Under these conditions the probability of the formation of surface protrusions is low and the granular microstructure is not developing. At high LDR, with a high flux of depositing species, shadowing overrules the anti-shadowing mechanism and the anomalous film growth leads to \( \kappa > 0 \), in the presence of surface protrusions. The origin of the seed protrusions can be either from irregularities present.
on pristine polymer, the result of the intrinsic random nature of the deposition process, or from oligomers formed in the gas phase migrating to the surface. In any case the presence of these seed protrusions will be enhanced at high flux of depositing species which leads to a higher probability of evolving surface protrusions. As a consequence the mean collision height cannot follow the surface asperities and shadowing prevails in the surface growth, thus developing a granular microstructure.

Moreover, the lateral grain growth that results in a grain-like microstructure in the high LDR region can lead to the formation of overhangs, thus forming a more porous structure as previously observed in [15]. Consequently the remedy for depositing smooth films is to reduce the probability of protrusions by reducing either the deposition time or the maximum LDR.

4. Conclusions

The SiO$_2$ film front growth has been studied, space and time resolved, in statically deposited thickness profiles synthesised in an AP-PECVD reactor. The rms roughness displayed an exponential scaling with the local film thickness, and a critical LDR of $7.2 \, \text{nm} \cdot s^{-1}$ was derived. The scaling behaviour of the surface roughness evolution was studied as a function of time for two positions in the reactor: at the maximum LDR with $LDR = 10.7 \pm 0.6 \, \text{nm} \cdot s^{-1}$ and in the centre of the reactor at the 0 position with $LDR = 5.4 \pm 0.6 \, \text{nm} \cdot s^{-1}$. The growth exponents $\beta$ have been calculated for both positions at the maximum LDR with $\beta = 0.33 \pm 0.05$ and at a lower LDR with $\beta = 0.11 \pm 0.02$. The dependence of $\beta$ on the LDR suggests a mechanism of surface roughening due to the formation of protrusions. It is considered that at higher LDR the probability of forming protrusions on the surface is increasing and as a result the roughness increases. Moreover, it can be concluded that the development of the growth front roughness can be controlled either by reducing the maximum LDR or by reducing the deposition time to achieve the desired film thickness under web rolled condition.

From the second order statistics it was found that the system exhibits an anomalous scaling behaviour characterized by values of $\alpha_s = 1.58 \pm 0.03$ determined from the PSDF, $\alpha_{loc} \approx 1$ obtained from the HHCF and the global roughness exponent $\alpha = 2.3 \pm 0.3$. The lateral grain growth and non-local interactions due to shadowing effects are proposed to be responsible for the anomalous scaling at a high flux of depositing species. Under the conditions of a low flux of depositing species a time invariant film growth is observed, as a result of the anti-shadowing mechanism. However, the anti-shadowing mechanism can be overruled at high flux of depositing species in the presence of surface protrusions, and subsequently shadowing may prevail, which results in the formation of a granular surface morphology.

This experimental finding is of interest from a fundamental perspective, as it elucidates the growth mechanisms in AP discharges, and from a practical point of view, as it opens new possibilities for growing conformal and smooth films.

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