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Citation for published version (APA):

Perrotta, A., Poodt, P., van den Bruele, F. J., Kessels, W. M. M., & Creatore, M. (2018). Characterization of nano-porosity in molecular layer deposited films. *Dalton Transactions*, 47(23), 7649-7655.
<https://doi.org/10.1039/C8DT01246F>

Document license:
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DOI:
[10.1039/C8DT01246F](https://doi.org/10.1039/C8DT01246F)

Document status and date:
Published: 01/05/2018

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Cite this: *Dalton Trans.*, 2018, **47**, 7649

Received 30th March 2018,
Accepted 9th May 2018

DOI: 10.1039/c8dt01246f

rsc.li/dalton

Characterization of nano-porosity in molecular layer deposited films†

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Molecular layer deposition (MLD) delivers (ultra-) thin organic and hybrid materials, with atomic-level thickness control. However, such layers are often reported to be unstable under ambient conditions, due to the interaction of water and oxygen with the hybrid structure, consequently limiting their applications. In this contribution, we investigate the impact of porosity in MLD layers on their degradation. Alucone layers were deposited by means of trimethyl-aluminium and ethylene glycol, adopting both temporal and spatial MLD and characterized by means of FT-IR spectroscopy, spectroscopic ellipsometry, and ellipsometric porosimetry. The highest growth per cycle (GPC) achieved by spatial MLD resulted in alucone layers with very low stability in ambient air, leading to their conversion to AlO_x . Alucones deposited by means of temporal MLD, instead, showed a lower GPC and a higher ambient stability. Ellipsometric porosimetry showed the presence of open nano-porosity in pristine alucone layers. Pores with a diameter in the range of 0.42–2 nm were probed, with a relative content between 1.5% and 5%, respectively, which are attributed to the temporal and spatial MLD layers. We concluded that a correlation exists between the process GPC, the open-porosity relative content, and the degradation of alucone layers.

Organic–inorganic hybrid thin films have been increasingly attracting the attention of the scientific community because they enable the design of new types of functional materials by combining organic and inorganic properties, yet differing from the properties of each of the pristine constituents.¹

Recently, molecular layer deposition (MLD) has been adopted to deliver either entirely organic or organic/inorganic hybrid (ultra-) thin films.^{2–4} In terms of the film growth mechanism, MLD is based on sequential and virtually self-lim-

iting reactions leading to films with atomic-level control and high conformality, in this aspect similar to atomic layer deposition (ALD). In the literature, several hybrid films have been reported, adopting a wide array of metallic elements (*e.g.*, Al,^{5–8} Ti,^{9,10} Zr,⁹ Hf,¹¹ Zn,^{12–15} V,¹⁶ Li,¹⁷ and Fe¹⁸). The organic co-reactant is usually a bifunctional organic molecule among which ethylene glycol (EG)⁴ or hydroquinone (HQ) is often reported.^{19,20} Generally, the films are referred to as ‘metal-cones’, *e.g.*, alucones, zincones, and titanicones.² However, while the self-limiting nature of the ALD process is based on the reactions of the precursor/co-reactant reactive species with available functional groups present exclusively on the surface, infiltration and sub-surface adsorption of the metal organic precursor in the growing layer have been reported during MLD growth.^{4,7,21,22} When this infiltration occurs, a CVD-like component has been found to contribute to the MLD film growth,^{4,7} driven by kinetic transport and diffusion effects instead of solely self-limiting surface reactions.²¹ Furthermore, when homo-bifunctional non-rigid (generally aliphatic) organic co-precursors are adopted, double reactions with the available functional groups on the surface have been reported, leading to limited or impeded growth of the MLD film in few cases.^{10,16,23}

Next to MLD fundamental growth mechanism studies,^{4,7,10,16,21–23} another major topic of investigation is MLD layer stability in ambient air.^{4,15,21,24} In the case of alucone layers, previous studies showed that the ones deposited using EG showed a thickness decrease, as witnessed by X-ray reflectivity,⁴ and micropore† formation, as detected by field effect-scanning electron microscopy,²⁵ already after few hours of exposure to atmosphere. The diffusion of water and oxygen in the film causes degradation of the alucone layer, which often results in hydrolization of the polymer chain groups and loss of thickness.^{4,23–25} Theoretical calculations confirmed the experimental results, showing the occurrence of spontaneous reactions of the infiltrated water with the hybrid polymer chains under ambient conditions.²⁵ In order to improve the stability of alucones, trifunctional (such as polyols)^{7,22} organic precursors have been adopted: the cross-

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c8dt01246f

linking of the polymer chains decreases the water accessible free volume of the hybrid MLD material, increasing its stability. Furthermore, the degradation caused by ambient species is delayed or even stopped, when capping the MLD films with inorganic layers. With this approach, alucone layers showed high stability over time and allowed, for example, their application as moisture barrier layers when coupled to inorganic layers.^{21,26,27} Consequently, the instability of MLD layers suggests the presence of open porosity accessible to ambient species.

In this contribution, the focus will be on MLD hybrid organic–inorganic materials, namely alucones. A complementary (to what has been reported so far in the literature) aspect of alucone degradation after exposure to atmosphere is investigated and the role of open porosity in ruling the degradation process is highlighted. Alucone layers, deposited at different growth per cycle (GPC) by trimethylaluminum (TMA) and EG, have shown different degradation rates, as followed by Fourier transform infrared spectroscopy (FT-IR) and spectroscopic ellipsometry (SE). A correlation was found between the GPC and the open porosity analyzed by ellipsometric porosimetry (EP)^{28–31} and finally correlated to the degradation process and rate.

The MLD depositions were performed in two different reactors at a substrate temperature of 100 °C. For the layers deposited at low growth per cycle, a home-built temporal MLD (t-MLD) reactor was adopted. For the spatial-ALD, a rotary spatial MLD (s-MLD) reactor was used, described in detail elsewhere.³² Trimethyl aluminum (TMA, electronic grade, AKZO HPMO) and ethylene glycol (EG, 99%, Millipore Sigma) were used as precursors and were evaporated using bubblers. TMA was kept at room temperature, while EG was kept at 80 °C.

The MLD cycle conditions are reported in Table 1. For the t-MLD process, different EG pulses were chosen in order to vary the GPC. All layers were deposited on *c*-Si wafers. During this process, the growth was followed by *in situ* spectroscopic ellipsometry (SE) by means of a J.A. Woollam, Inc. M2000F ellipsometer at an angle of incidence of 70°, in the spectral range of 246–1000 nm. The alucone layers were modeled using a Cauchy function. For each sample, the error bar on the refractive index was estimated ± 0.003 .

In order to obtain layers deposited at very high GPC, spatial MLD was adopted. Polished silicon wafers (6" diameter) were used as substrates. The deposition was performed at 30 rotations per minute (rpm) resulting in a GPC of 2.7 nm per cycle. The exposure and purging times vary radially between

70 ms and 250 ms. The analyzed samples were deposited with an exposure/purging time of 160 ms. All layers were stored under an inert atmosphere (N₂).

The opto-chemical characterization of thin films after exposure to the atmosphere was performed with *ex situ* SE and FT-IR. SE measurements were carried out with a J.A. Woollam, Inc. M2000D system at angles of incidence of 60°, 70°, and 80° in the spectral range of 246–1000 nm. FT-IR measurements were performed with a Bruker Tensor 27 spectrophotometer in the range of 375–4000 cm^{−1} with a resolution of 4 cm^{−1} and 512 scans. All the reported FT-IR spectra are baseline corrected and normalized with respect to the layer thickness.

The relative amount of open porosity in the hybrid layers was determined by means of EP immediately after deposition. EP provides information on the open porosity and pore size distribution present in the layers.^{31,33} It relies on the change of the optical properties of the film during vapor adsorption and desorption. The adsorption of probe molecules leads to a variation of the refractive index (*n*) and the development of an adsorbate multilayer, both of which are monitored by SE. Classical adsorption/desorption isotherms can be obtained by plotting the variation of the optical properties as a function of the relative pressure, defined as the ratio between the equilibrium partial pressure (*P*_i) and the vapor pressure (*P*_{sat}) of the probing liquid as measured at room temperature.^{31,33,34} In order to probe pores with different diameters, two probing molecules, toluene and ethanol, were adopted having a molecular diameter of 0.6 nm and 0.43 nm, respectively. The probe molecule multilayer uptake was fitted by adding a Cauchy layer on top of the alucone layer with a fixed refractive index of the adsorptive, and with its thickness being the only fitting parameter. More details on the technique and experimental setup can be found in ref. 28–35.

For the temporal processes, the growth rate observed at the high EG exposure (6.5 s) is similar to values reported by Dameron *et al.*⁴ for saturated processes determined using a quartz crystal microbalance at the same temperature (0.25 nm per cycle). However, in our case, no saturation regime was observed by *in situ* ellipsometry under the experimental conditions explored, due to the bubbler configuration adopted, which did not allow enough EG to completely saturate the surface. In the literature, different GPCs are reported under saturation conditions. Park *et al.*²³ reported a GPC of 0.24 nm per cycle for MLD alucone layers when deposited at a higher temperature, 120 °C, while in the work of Dameron *et al.*, the GPC is found to drastically decrease as a function of tempera-

Table 1 MLD conditions adopted in the temporal and spatial mode

	TMA dose	Purging TMA	EG dose 3.5 s	Purging EG	Pressure
Temporal	50 ms	2 s	6.5 s	60 s	10 ^{−2} mbar
	Rotation per minute	Exposure time	Purging time	Pressure	
Spatial	30 rpm	70–250 ms	1.85–1.5 s	Atm. pressure	

Table 2 GPC, optical and porosity characterization of the MLD layers under study. All the *ex situ* refractive index values were measured after few minutes of exposure to the atmosphere

	GPC	$n_{in\ situ}^a$ (± 0.003)	$n_{ex\ situ}^a$ (± 0.003)	Porosity pore diameter ≥ 0.6 nm ($\pm 0.2\%$)	Porosity pore diameter ≥ 0.42 nm ($\pm 0.2\%$)
Spatial MLD	2.72 nm per cycle	—	1.513	3%	5%
Temporal MLD	0.23 nm per cycle (with EG pulse 6.5 s)	1.487	1.507	2.7%	3.9%
	0.14 nm per cycle (with EG pulse 3.5 s)	1.505	1.503	1.5%	3.2%

^a Measured at 633 nm.

ture. Furthermore, Park *et al.* reported DFT calculations of the theoretical thickness of one monolayer of alucone deposited by EG and TMA, found to be equal to 0.53 nm. The lower GPC was then attributed to specific orientation of the EG molecule when bound to the growing surface. Finally, Choi *et al.*²⁵ reported on a GPC at 100 °C slightly below 0.4 nm per cycle. These variations show that, although all cited studies reported on saturated processes, other experimental factors might affect the GPC values, such as exposure times, working pressure, and purging times.

The refractive index values measured *in situ* (Table 2) point out that a denser film develops when deposited at a lower GPC. The lower value of the *in situ* refractive index, together with the increased GPC, suggests the development of a disordered film when higher EG exposure times are selected, or, alternatively, there is contamination in the form of short oligomers. A CVD-like contribution to the overall growth is hypothesized under the explored condition, in line with what reported in the literature for TMA-based MLD processes, as afore-mentioned.^{4,21,22} Additionally, in other *in situ* SE investigations on MLD growth mechanisms, Van de Kerckhove *et al.*^{10,16} recently reported the deposition of V- and Ti-based metalcones, showing the saturation behavior of both organic and metalorganic precursors. They showed that, adopting EG as a co-reactant, the MLD film growth stopped after a few cycles, suggesting the dominance of double reactions at the surface hindering the growth, while saturation was reached adopting glycerol as a co-reactant. In our studies, *in situ* ellipsometry measurements showed a constant linear increase in thickness for all the cycles and processes investigated (see the ESI†). Nevertheless, the use of metalorganic precursors with a higher steric hindrance than TMA (0.65 nm in diameter, compared to 1 nm in diameter of the Ti- and V-based precursors used in ref. 10 and 16)§ might lead to different growth mechanisms, considering that the sub-surface infiltrated TMA molecules have been shown to participate in the film growth.

The *ex situ* refractive index measured within a few minutes of exposure to ambient air for both s-MLD and t-MLD layers is reported in Table 2. For the t-MLD layers, the one deposited at the lowest GPC showed no significant variation of the refractive index. The high GPC t-MLD layer, instead, showed an increase of the refractive index value of 0.02. This difference is attributed to the adsorption of water vapor in pores accessible to water molecules³³ (*i.e.*, with a diameter equal to or higher

than the kinetic diameter of water, 0.27–0.33 nm).³⁶ The s-MLD layer showed the highest $n_{ex\ situ}$ value, pointing out a higher amount of pores accessible to water and, in turn, suggesting a more porous nature of the s-ALD alucone layer compared to the t-MLD layers.

Alucone layers deposited with TMA and EG have been reported to undergo degradation upon ambient exposure due to the reaction of the hybrid chains with water, as afore-mentioned. In order to follow the MLD layer degradation, the refractive index and thickness were followed in time after exposure to ambient air by *ex situ* SE measurements (Fig. 1). The two t-MLD layers showed a decrease in the refractive index in time (Fig. 1a). The decrease is due to the hydrolysis of the hybrid chains followed by desorption of C-containing volatile species,^{14,25} which eventually leads to an increase in the overall porosity of the layers, and thus to a decrease in the refractive index.²⁵

The layer deposited with s-MLD showed a similar decrease in the first hour of exposure. Afterwards, the refractive index was found to increase. Furthermore, by following the thickness loss as a function of time, all layers were found to lose between 15% and 30% of their thickness (Fig. 1b). The s-MLD layer shows an abrupt loss of material in the first 2 hours of exposure, which might lead to a collapse of the layer and cause the increase in the refractive index. Furthermore, both the conversion of the layer to AlO_x (as a reference, n of ALD thin alumina films deposited at 100 °C is in the range of 1.56–1.64 at 633 nm)^{33,37} and a further water vapor adsorption in the newly developed porosity can contribute to the refractive index increase. The layers deposited at lower GPC showed a lower thickness loss rate, indicating a higher stability when compared to the highest GPC deposited layer. In the first hour, the

Fig. 1 (a) Refractive index measured *ex situ* and (b) thickness loss measured using SE as a function of exposure time to the atmosphere.

t-MLD layers showed no loss in thickness, pointing out that the initial formation of the porosity/hydrolysis process is not sufficient to cause major changes in the structure of the layer. Instead, within 4 h, a total decrease in thickness of 30% is observed. Dameron *et al.*⁴ reported a thickness loss of approximately 5% in the first hours, up to 20% in the first 200 h of exposure to the atmosphere for an alucone layer deposited at 135 °C using TMA and EG. The difference in the thickness loss rate might be attributed to the higher deposition temperature in the work of Dameron,⁴ as well as differences in EG and TMA exposure times. The latter could play a role in the diffusion of TMA in the sub-surface of the growing layer, and therefore on the structure of the hybrid layer. Furthermore, Choi *et al.*²⁵ showed a steady thickness loss over the first 1000 min of exposure to the atmosphere for an alucone deposited at 90 °C, up to 40% of the initial thickness. Considering the high GPC reported (0.4 nm per cycle), this result confirms the difference in stability, and, in turn, in the growth mechanism as a function of the GPC.

In order to quantify the open-porosity content, EP measurements were carried out. In Fig. 2, the adsorption/desorption isotherms are reported as a ratio between the volume of the adsorptive and the volume of the film ($V_{\text{ads}}/V_{\text{film}}$), as a function of the partial pressure of the probing molecule (P/P_{sat}), in line with our previous publications.^{29,35}

In Fig. 2a, the isotherms are obtained by measuring the layers adopting toluene as a probing molecule. The adsorptive uptake was expressed as adsorptive volume. From the Lorentz–Lorenz relationship, the adsorptive volume in pores can be calculated as:

$$V_{\text{ads}}/V_{\text{film}} = V_{\text{mol}}/[(\alpha_{\text{ads}} \cdot (d_t + d_0)) \cdot ((B_s d_0 + B_t d_t) - B_0 d_0)] \quad (1)$$

where V_{ads} is the volume of the adsorptive liquid in pores, B_0 and B_s are the volume polarizability of the film before and during adsorption, B_t is the volume polarizability of the adsorbate multilayer that develops on top of the layer, d_0 and d_t are the thicknesses of the layer and the adsorbate multilayer, respectively, V_{mol} is the molecular volume of the adsorptive, and α_{ads} is the polarizability of the adsorptive molecule.

Fig. 2 Adsorption/desorption isotherm measured using EP for the MLD layers adopting (a) toluene (0.6 nm in diameter) and (b) ethanol (0.42 nm in diameter). The solid and empty symbols describe the adsorption and desorption branches, respectively. The error on the porosity value is 0.2%.

Therefore, the adsorptive volume contains both information about pore filling and multilayer formation.

The porosity (P) is calculated using the Lorentz–Lorenz equation. P can be expressed as:

$$P = \left[\frac{(n_{\text{fill}}^2 - 1)}{(n_{\text{fill}}^2 + 2)} - \frac{(n_0^2 - 1)}{(n_0^2 + 2)} \right] / \left[\frac{(n_{\text{vapor}}^2 - 1)}{(n_{\text{vapor}}^2 + 2)} \right] \quad (2)$$

in which n_0 and n_{fill} are the refractive index values of the layer when the pores are either empty or filled, respectively, and n_{vapor} is the refractive index of the probe molecule. With this approach, the nano-porosity values obtained are independent of the refractive index of the matrix.

All layers showed a nano-porous nature and no swelling was detected, *i.e.*, the layer thickness stayed constant during adsorption/desorption processes and only the multilayer formation of the probe molecule was measured. Below P/P_{sat} of 0.2, all layers showed a similar nano-pore content, determined to be 1% with eqn (2). This region is generally attributed to the so-called nano-pore filling, *i.e.*, when all nano-pores with diameter in the range of the one of the probe molecules are filled. Above P/P_{sat} of 0.2, the adsorption further develops, indicating a broad range of nano-pores with a diameter between 0.6 (in the case of toluene) and 2 nm. The main differences among the layers are detectable at high P/P_{sat} values, *i.e.*, above 0.7. Adsorption in this region is attributed to pores with the diameter close to the nano-porosity limit of 2 nm and/or to the formation of the probe molecule multilayer. For the s-MLD layer, this increase in toluene adsorption is caused by an increase in the refractive index, which points out a higher porosity. In the case of the t-MLD layers, instead, the increase in $V_{\text{ads}}/V_{\text{film}}$ is mostly due to the formation of a multilayer. In microporous materials showing low values of porosity, the multilayer formation starts already at a low value of P/P_{sat} , due to the high outmost surface area, contributing to the overall probe molecule adsorption.³³ The porosity content was measured from the value of the refractive index at the end of the adsorption process applying eqn (2), *i.e.*, when all the pores accessible to the probe molecules are filled. The porosity values are reported in Table 2 and show differences in porosity as a function of the GPC. The alucone deposited at the lowest GPC value showed the smallest amount of open porosity accessible to toluene, *i.e.*, with a diameter ≥ 0.6 nm. Furthermore, all layers showed hysteresis in the desorption branch, due to the interaction of the probe molecule with the backbone chains of the MLD layer. The t-MLD layer with the highest GPC showed the largest hysteresis and it can be attributed to the presence of tortuosity and interconnected pores, trapping the probe molecules and hindering their desorption. It is worth mentioning that a classical pore size distribution for nanoporous layers could also be obtained adopting the Dubinin–Radushkevich–Stoeckli (DRS) equation.³⁸ However, the low value of porosity detected, together with the assumptions in terms of pore shape and adsorbate–pore wall interaction to be made, make the DRS not suitable for the layers presented here.

In order to better highlight differences in porosity content, the layers have also been measured adopting ethanol as a probe molecule, therefore detecting pores with a diameter ≥ 0.43 nm. The adsorption/desorption isotherms are presented in Fig. 2b. Also in this case, the layers show similar values of porosity in the nano-pore filling region. Differences arise above P/P_{sat} of 0.2, thus suggesting a broad range of pore diameter also between 0.43 nm and 0.6 nm. The pore content values are reported in Table 2. As in the case of toluene, the porosity values scale with the GPC: the layers deposited at a lower GPC showed the least amount of open pores accessible to ethanol. Furthermore, it can be concluded that the high-GPC t-ALD layer differs from the s-ALD alucone primarily in terms of the small pore size relative content (*i.e.*, pores with diameter between 0.4 and 0.6 nm). Hysteresis was found for all layers in the desorption branch. In this case, the amount of hysteresis follows the porosity trend, pointing out the presence of interconnected and tortuous porosity in the range of diameter 0.43–0.6 nm.³⁹

In summary, the GPC was found to correlate with the amount of nano-porosity in the layers, and, considering that EP allows the detection of open-pores, the measured nano-porosity was found to be accessible to water and oxygen molecules. Higher GPCs lead to less ordered alucone structures, in turn suggesting differences in growth mechanism as a function of the growth per cycle. Consequently, as a function of the GPC, a higher amount of water and oxygen molecules is allowed to permeate through the alucone layer, enhancing its degradation rate upon exposure to the atmosphere.

In the literature, EP measurements on MLD layers have been performed on titanicones¹⁰ and vanadicones¹⁶ adopting toluene as a probing molecule. In these contributions, no porosity accessible to toluene vapors was detected. As aforementioned, the Ti- and V-based precursors showed a self-limited behavior. Moreover, the use of a triol (*i.e.*, glycerol) as a co-precursor has been shown to lead to more stable cross-linked hybrid materials, accounting for the absence or limited presence of porosity. Specifically, porosity below 0.6 nm in diameter cannot be probed by toluene, suggesting the possible presence of smaller pores, as reported in the present study.

In order to additionally verify the chemical and structural changes of the pristine layers and upon exposure to the atmosphere, FT-IR measurements were performed on the t- and s-MLD layers as a function of the atmosphere exposure time, and are reported in Fig. 3.

The spectra at 0 h of exposure to the atmosphere show a higher degree of oxidation/water uptake for layers deposited at high GPC (Fig. 3b and c) compared to the t-MLD layer deposited at lower GPC (Fig. 3a), in agreement with SE and EP measurements. Comparing the AlO stretching band at 902 cm^{-1} and the hydroxyl (–OH) absorption between 3000 and 3300 cm^{-1} , the amount of Al–OH groups is larger for high GPC deposited layers and relates to porosity, the –OH group being either attributed to hydrolyzed sites or terminating glycol chains. Furthermore, adsorbed water and isolated –OH groups account for the absorption in the 3300–3600 cm^{-1}

region, corroborating the differences in porosity among the layers.³³ FT-IR then confirms the hypothesis of a different chemical composition and microstructure and, in turn, a different growth mechanism as a function of the GPC for MLD deposited alucones.

In order to investigate how the presence and the relative content of open porosity control the degradation mechanism of the MLD layers, FT-IR measurements were performed as a function of the exposure time to ambient air. In Fig. 3, the FT-IR spectra of alucones in the first 4 hours of exposure to air are reported. The spectra reveal an increase in the –OH stretching adsorption in the 3000–3600 cm^{-1} region. Moreover, a broad peak arises between 1400 cm^{-1} and 1650 cm^{-1} , attributed to the formation of enolate-type vinyl ether species, in agreement with the literature.^{4,24,25} In addition, the decrease of the absorption attributed to the C–O vibrational stretching at 1086 cm^{-1} and the formation of a broader peak between 740 cm^{-1} and 500 cm^{-1} point out the loss of carbon-containing functionalities and the contemporary increase of AlO_x groups, more pronounced for the s-MLD layer, suggesting the formation of an alumina-like structure, as witnessed by SE. The loss of C-containing groups is confirmed by the decrease of the CH_x stretching adsorption in the range of 2800–3000 cm^{-1} . As observed in Fig. 3, the degradation of the alucone layers correlates with the porosity content in the layer inferred by SE and EP. The layer deposited at the lower GPC with t-MLD showed the lowest amount of degradation in terms of the formation of –OH groups, C-containing group loss, and the formation of enolate-type vinyl ether species. In contrast, the layer deposited with s-MLD, *i.e.*, at the highest GPC, showed the highest degree of degradation. The CH_x and C–O stretching absorption are found to quantitatively decrease as a function of the exposure time to the atmosphere, pointing out the desorption of volatile C-containing species from the hybrid backbone and the almost complete conversion to an AlO_x layer. It is worth noticing that, while the –OH group formation rate is faster for the s-MLD layer, the final –OH adsorption band is more intense for the t-MLD layer deposited at a high GPC. This discrepancy might be due to the simultaneous contribution to the –OH band of the adsorbed water vapor and chain terminating –OH groups, considering that the ratio between the AlO and the –OH stretching band points out the presence of more AlOH groups in the s-MLD compared to the t-MLD.

In summary, alucone layers were deposited by means of spatial and temporal MLD and ellipsometric porosimetry measurements allowed the detection of open, small nano-porosity (*i.e.*, between 0.42 and 0.6 nm) in the MLD alucone layers. By following the degradation of the layers as a function of time, a correlation was found between the GPC and the stability of the alucone layers, due to the different porosities accessible to ambient species such as water vapor and oxygen. FT-IR spectra pointed out to a difference in the chemical composition and the degradation rate when comparing spatial and temporal MLD alucone layers. Layers deposited with s-MLD showed a strong decrease of C-containing groups and the for-

Fig. 3 FT-IR measurements as a function of the exposure time to the atmosphere for (a) low GPC t-MLD layer, (b) high GPC t-MLD layer, and (c) s-MLD layer. In the table, band assignment of the FT-IR spectra. Ads: adsorbed, ν: stretching mode, δ: bending mode.

mation of alumina-like structures, as also pointed out by the increase in the refractive index as measured by SE. Differences in layers' porosity are pointed out by the different initial amount of chain terminating -OH groups and by the overall conversion to AlO_x, more pronounced for the s-MLD layer, as witnessed by the strong decrease in CH_x and C-O stretching absorption. Moreover, considering that the major differences in porosity were found with respect to the amount of pores with a diameter above 0.6 nm as measured by EP, we can conclude that these pores are primarily responsible for the faster degradation of the s-MLD alucone layers. t-MLD layers still showed degradation upon exposure to the atmosphere, due to the presence of nano-pores with a diameter accessible to water (>0.3 nm). Although it is not possible to quantify the CVD-like component in the alucone process, this study highlights the role of faster and less ordered growth in affecting the porosity and, in turn, the stability of the layers. Further studies need to be performed in order to identify process parameters such as precursor exposure, purging time, and pressure in affecting the growth and therefore the stability of the layers.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors would like to thank J. J. A. Zeebregts, J. J. L. M. Meulendijks, and C. O. van Bommel (Eindhoven University of Technology) for their skillful technical assistance.

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‡ Microporosity (also referred as nano-porosity) comprises pores with a diameter ≤2 nm. Pores with a diameter >2 nm are instead considered meso-pores.^{28,40}

§The molecular dimensions were obtained optimizing the geometry using an MM2 force field and calculating the cross section with Mol2Mol® software.

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