Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

On the role of micro-porosity in affecting the environmental stability of atomic/molecular layer deposited $(ZnO)_a(Zn\text{-}O\text{-}C_6H_4\text{-}O)_b$ films

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Supporting Figures

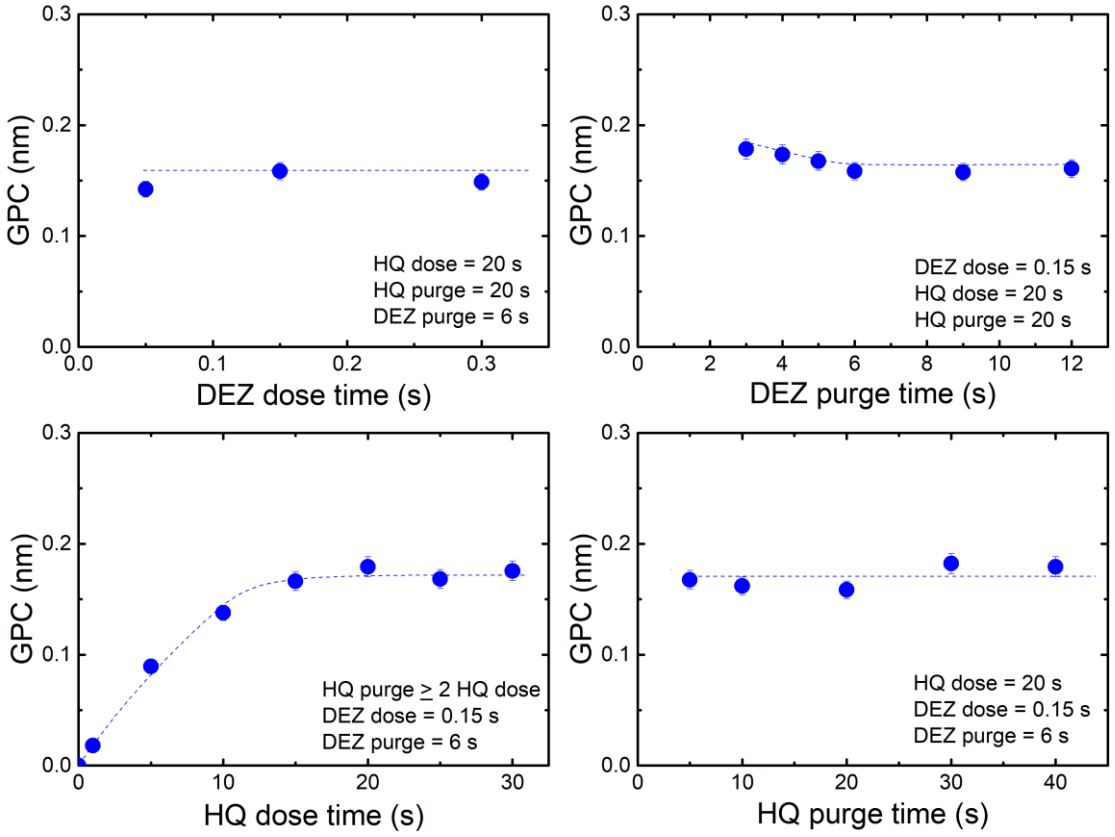

Figure S1. Saturation curves for zincone MLD process, measured by *ex*-situ spectroscopic ellipsometry. Lines serve as guides to the eye.

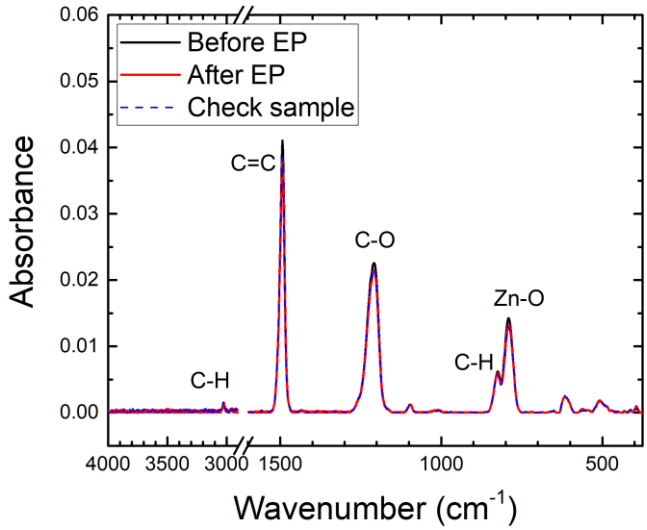

Figure S2. FTIR spectra of a 60 nm as-deposited zincone film before and after EP measurement (12 hours in vacuum after the measurement). The intensity of the main absorption peaks in the zincone film after EP are slightly lower than the as-deposited film, which is most probably related to the degradation of the film during a few minutes exposure of the samples to the environment when transferring from FTIR setup to the EP chamber and back. In order to check this, a sample (check sample) was exposed to air for a similar amount of time. The intensity of the peaks in the sample after EP is similar to the check sample.

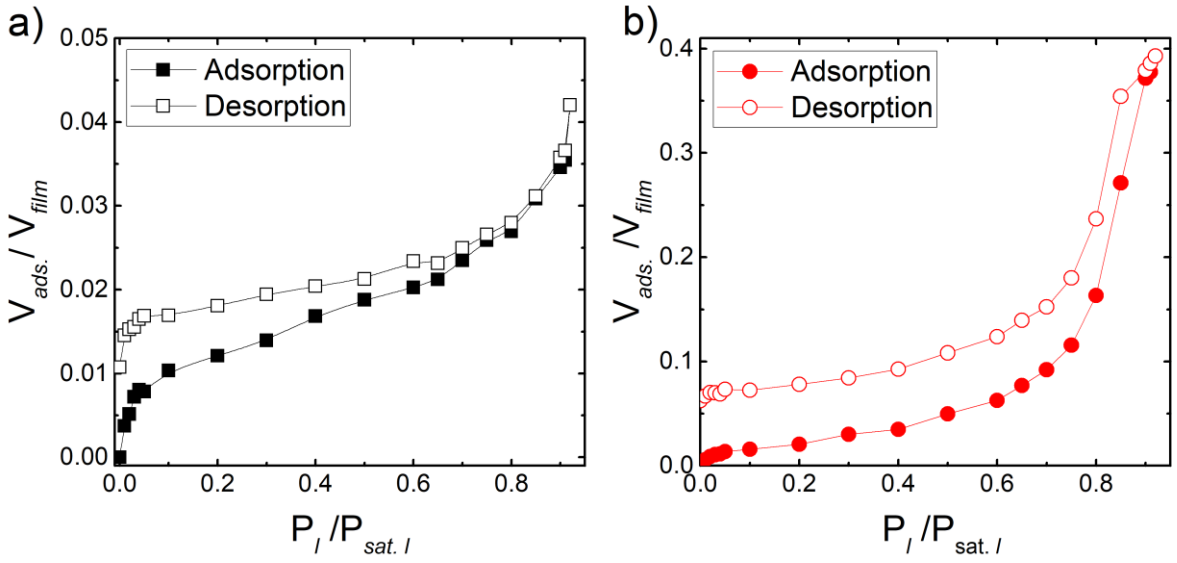

Figure S3. Ethanol adsorption and desorption isotherms of a) pristine zincone (73 nm) and b) the zincone sample after 1 day in ambient air. In the both cases, desorption is complete, i.e. $V_{ads.}/V_{film} = 0$ at $P_l/P_{sat.} = 0$, upon 12 hours under vacuum (not shown in the graphs). This also allows to conclude that no change occurs in the film upon EP measurements.

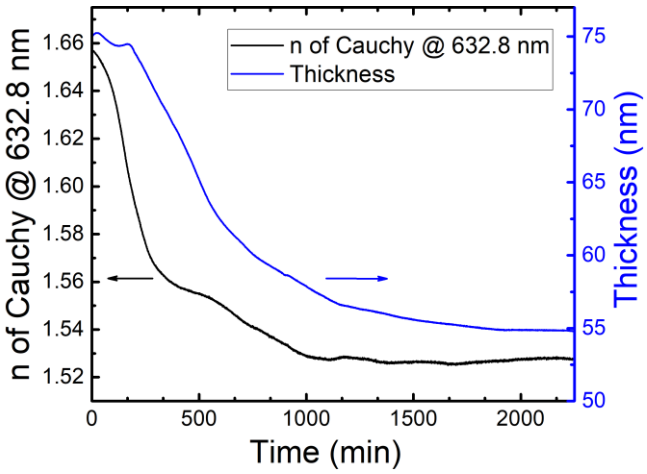

Figure S4. Real time spectroscopic ellipsometry analysis of zincone in ambient air (22 ˚C, 58 % RH). The measurement step was 30 s.

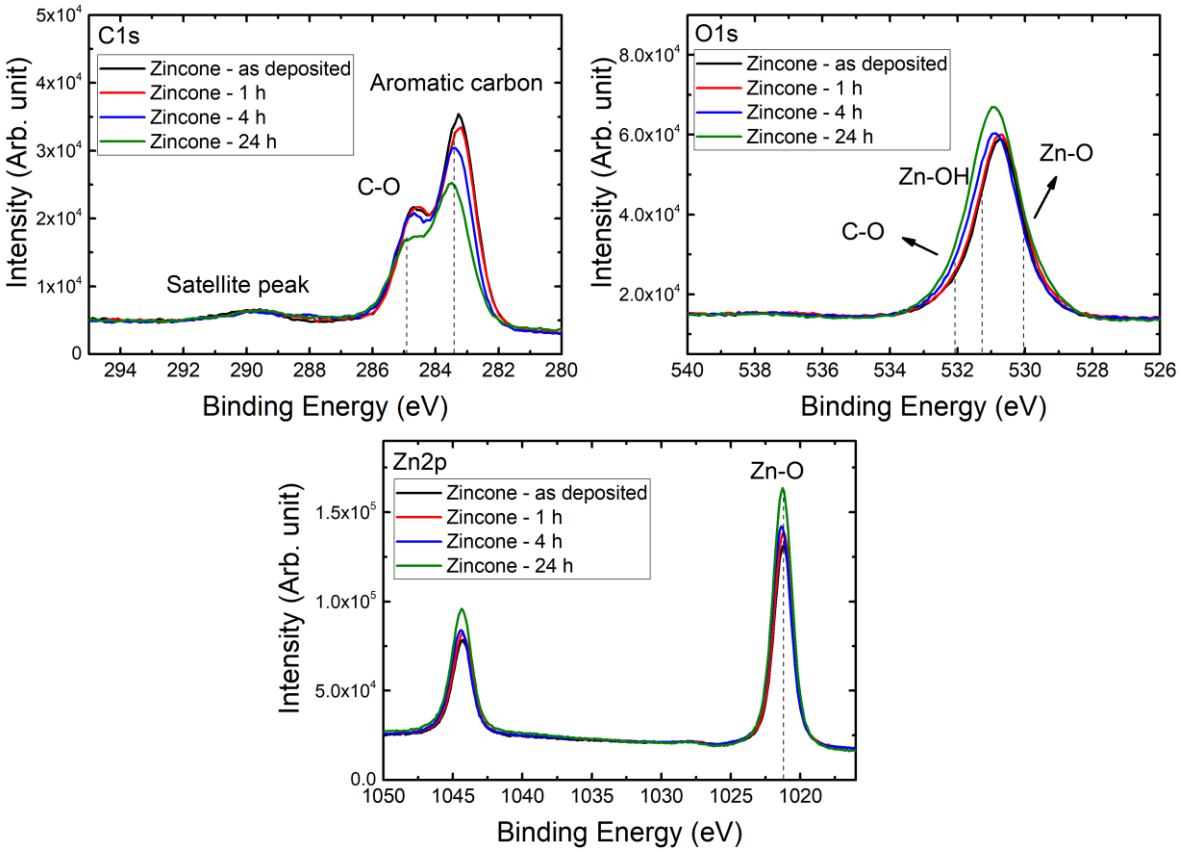

Figure S5. High resolution C1s, O1s and Zn2p XPS spectra of as-deposited and degraded zincone films. Thickness of the as-deposited film is 65 nm.

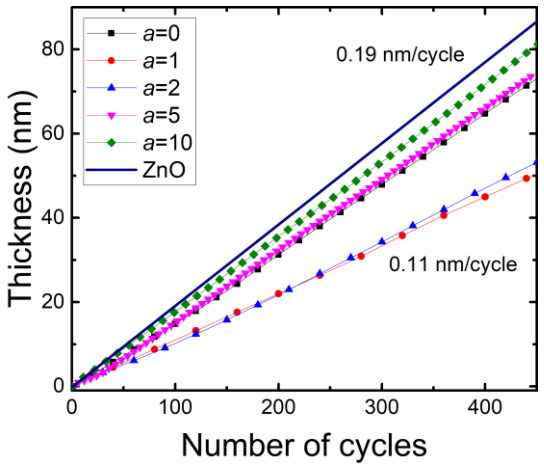

Figure S6. Thickness of $(ZnO)_a(Zn\text{-}O\text{-}C_6H_4\text{-}O)_{b=1}$ films measured during ALD/MLD process by *in-situ* ellipsometry measured after every 5-20 cycles.

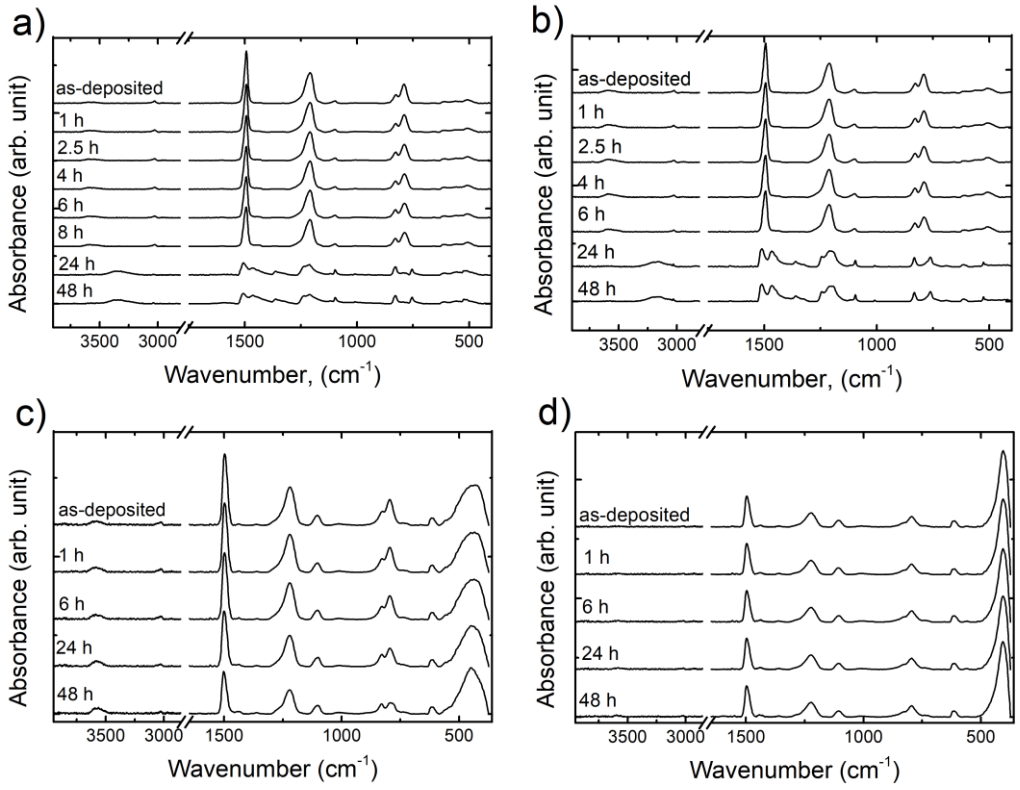

Figure S7. FTIR spectra of $(ZnO)_a(Zn\text{-}O\text{-}C_6H_4\text{-}O)_{b=1}$ layers with *a* values equal to a) 1 (79 nm) , b) 2 (88 nm), c) 5 (84 nm) and d) 10 (85 nm) in as-deposited state and after degradation in ambient air. Thicknesses were measured by *in-situ* SE after deposition and before unloading the samples from the reactor. The peaks assignments are available in Table 2.

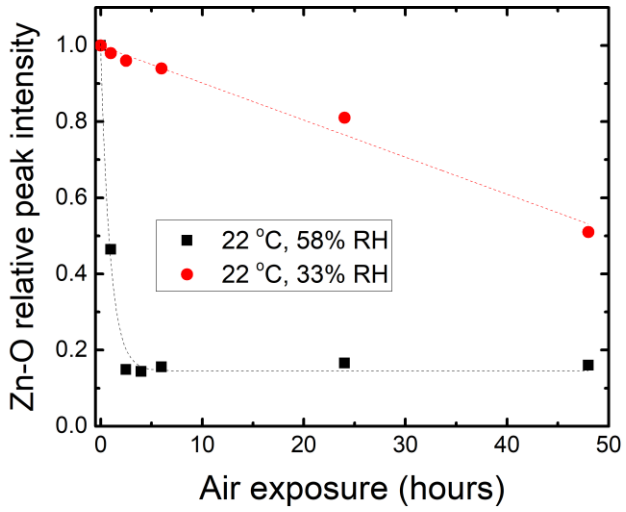

Figure S8. Relative intensity of the Zn-O FTIR peak at 788 cm^{-1} for a zincone (73 nm) film at two different environments.

Supporting tables

Table S1. Chemical composition of $(ZnO)_a(Zn\text{-}O\text{-}C_6H_4\text{-}O)_{b=1}$ layers measured by RBS/ERD. Thickness of the layers were measured by SE and used in the mass density calculations. The relative errors (combined statistical and systematical errors) for C and O: 5%, Zn: 3%, H: 9%. The maximum error in the mass density calculation is 9%. The error in the thickness values is typically < 1 nm.

a in $(ZnO)_a(Zn\text{-}O\text{-}C_6H_4\text{-}O)_{b=1}$	Thickness (nm)	Atomic %				Mass density ($g \cdot cm^{-3}$)
		[H]	[C]	[O]	[Zn]	
0 (Zincone)	65	24.7	48.1	18.4	8.8	1.95
2	88	28.1	38.6	21.8	11.5	2.31
5	84	15.5	20.1	35.2	29.2	4.17
10	85	11.8	13.4	38.4	36.4	4.65
ZnO	70	2.1	3.1	48.1	46.7	5.49

Electrical properties

Stemming from the general interest towards ZnO for various optoelectronic applications, the transport properties of these Zn-based ALD/MLD hybrids are of interest.[1,2] In the case of $(ZnO)_a(Zn\text{-}O\text{-}C_6H_4\text{-}O)_{b=1}$ type multilayers, we observed an onset (measurability with a four-point probe) in electrical conductivity for multilayer compositions with $a \geq 10$. The previous reports have given contradictory results in terms of electrical conductivity: high conductivity has been observed already for small $a \sim 1$,[2] but larger a values ~ 40,[3] have been also reported to be required for onset in conductivity. In our study, as the samples with small a (< 10) were found too resistive to be measured with the four-point method, samples with $a = 20$ and $a = 50$ were studied as well. We observed that for $a \geq 20$, resistivity ($\rho = (ne\mu)^{-1}$, where n is the carrier density, e the elementary charge and μ the mobility) was similar to that of purely inorganic ZnO, while for $a = 10$ resistivity increased notably (**Table 4**). Hall measurements indicated that this increase in resistivity was due to decrease in both n and μ. Moreover, within the sample series studied, any remarkable benefits to electrical transport were not identified by incorporation of aromatic units in ZnO. This is in contrast to what was observed by Yoon *et al.*[2] and in line with results by Tynell *et al.*[3] Note that the conductivity of our intrinsic ZnO was already at the level of the most conductive hybrid films by Yoon et al.[2], which could make further increase in conductivity challenging.

Table S2. Resistivity (ρ), carrier electron density (n) and mobility (μ) obtained *via* Hall measurements for the $(ZnO)_a(Zn\text{-}O\text{-}C_6H_4\text{-}O)_{b=1}$ films. The samples with a ≤ 5 were too resistive to be measured with the four-point method. The error in the thickness values is typically < 1 nm.

Sample	**Thickness (nm)**	**ρ (10^{-3} Ωcm)**	**n (10^{19} cm^{-3})**	**μ (cm^2/Vs)**
ZnO	66	7.8±0.1	2.8±0.1	28.9±2
***a* = 50**	98	6.9±0.1	2.9±0.1	31.3±2
***a* = 20**	103	9.0±0.1	3.1±0.2	22.1±1
***a* = 10**	85	(12.3±0.2)×10^3	0.01±0.005	0.5±0.1

References

(1) Niemelä, J.-P.; Karttunen, A. J.; Karppinen, M. Inorganic–organic Superlattice Thin Films for Thermoelectrics. *J. Mater. Chem. C* **2015**, *3* (40), 10349–10361.

(2) Yoon, B.; Lee, B. H.; George, S. M. Highly Conductive and Transparent Hybrid Organic − Inorganic Zincone Thin Films Using Atomic and Molecular Layer Deposition. *J. Phys. Chem. C* **2012**, *116*, 24784−24791.

(3) Tynell, T.; Karppinen, M. ZnO: Hydroquinone Superlattice Structures Fabricated by Atomic/Molecular Layer Deposition. *Thin Solid Films* **2014**, *551*, 23–26.