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Atomic/molecular layer deposition: a direct gas-phase route to crystalline metal-organic framework thin films

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Atomic/molecular layer deposition offers us with an elegant way of fabricating crystalline copper(II)terephthalate metal-organic framework (MOF) thin films on various substrate surfaces. The films are grown from two gaseous precursors with a digital atomic/molecular level control for the film thickness under relatively mild conditions in a simple and fast one-step process.

Metal-organic framework (MOF) materials are made of inorganic cations and organic linkers to yield crystalline highly porous structures. Such materials are demanded in a number of frontier applications for e.g. gas separation, drug release, catalysis and sensors.¹⁻⁴ They are also highly resistant to structural collapse upon gas evacuation which makes them excellent hosts for safe and effective gas storage, thus placing them interesting material candidates to be exploited in e.g. fuel cells and other next-generation energy technologies.⁵⁻⁸ Many of the future applications would require the MOF materials in thin-film form, though.

Thin MOF films have been produced mostly with solution techniques such as immersion, spin coating and dip-coating techniques;⁹⁻¹¹ yet to be exploited is the fabrication of these materials in a highly controlled way from gas phase which would allow e.g. the deposition of thin conformal MOF coatings over porous or other geometrically challenging surfaces such as nanotubes. The currently strongly emerging combined atomic/molecular layer deposition (ALD/MLD) technique for inorganic-organic hybrid thin films would provide us with a number of uniquely exciting features. The technique relies on self-saturating gas-to-surface reactions that guarantee the thin-film fabrication with atomic/molecular monolayer precision; for recent comprehensive review see Ref. 12 and the references therein. The technique has however not yet been employed to produce crystalline MOF films as only amorphous inorganic-organic hybrid films have been reported so far. Recently, MOF structures were reported for

amorphous films initially grown by ALD/MLD after a two-step post-deposition annealing treatment under strictly humidity-controlled conditions.^{13,14} Here we report for the first time a simple direct ALD/MLD route for fabricating highly crystalline copper(II)terephthalate (Cu-TPA) MOF thin films, using 1,4-benzenedicarboxylic (1,4-BDC) or so-called terephthalic acid (TPA) as the organic precursor.

Bulk MOF materials with the same TPA precursor have been fabricated using at least Cr, In, Zn, Al and Cu as the metal constituent by conventional bulk methods.^{3,15,16} As for the potential applications, Cu-based MOFs have been studied for sponge-like magnets,¹⁷ and electrocatalysis¹⁸ and also as highly sensitive skeleton for selective sensors for important amino acids.¹⁹ The copper(II)terephthalate MOFs exhibit additionally a notable stability towards aqueous solutions.²⁰ Moreover, high surface areas induced by massive amounts of pores have also been reported.^{21,22}

From bulk studies it is known that copper(II)terephthalate has a lamellar MOF-2 type paddlewheel structure similar to that of copper(II)*trans*-1,4-cyclohexanedicarboxylate; unfortunately high-quality single crystals have not been available so far for a more precise crystal structure determination.²³⁻²⁶ The paddle-wheel structure is constructed from two copper atoms which are linked by four terephthalate groups, as illustrated in Fig. 1. Two-dimensional paddlewheel sheets stack on top of each other forming a network of holes which align perpendicularly to the surface,^{6,24} although calculations indicate affinity for a more ordered stacking.²⁶ By changing the size of the carboxylate molecules, the pore size can be controlled up to some nanometers.²⁶

The Cu-TPA films were successfully grown in a commercial ALD reactor (F-120, ASM Microchemistry Ltd.) from Cu(thd)₂ (copper 2,2,6,6-tetramethyl-3,5-heptanedione; prepared in-house²⁷) and terephthalic acid (Tokyo Chemical Industry CO., Ltd, CAS: 100-21-0) precursors; the precursor sublimation temperatures were fixed at 110 and 180 °C, respectively, based on our preliminary data from thermogravimetric analysis (Perkin-Elmer TGA 7) and observed sublimation rates in our

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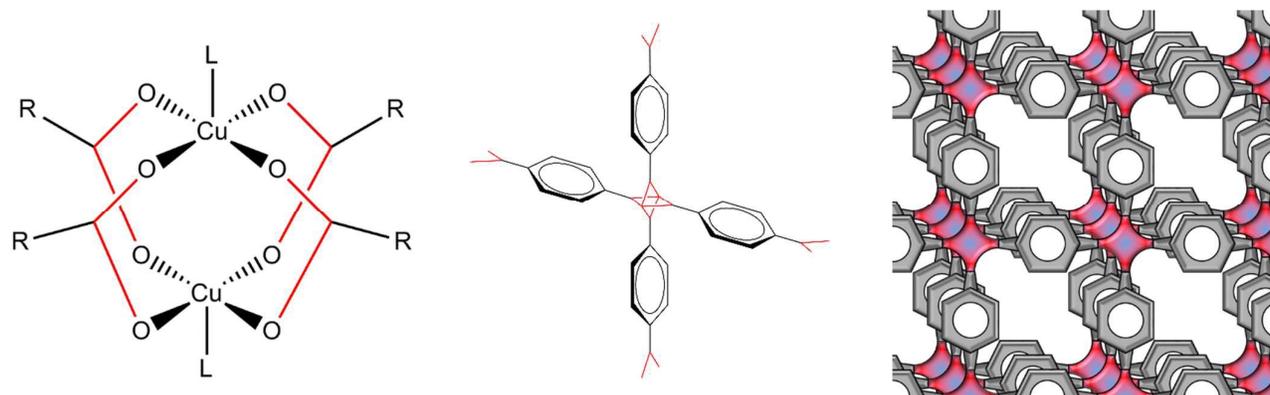


Figure 1: Paddlewheel structure associated to copper(II)terephthalate MOF materials; R corresponds to the terephthalate and L is a coordination site.

F-120 reactor. Nitrogen (99.999 %, 300 sccm; Schmidlin UHPN 3000N generator) was used as the carrier and purge gas in the depositions with the background pressure of ca. 2–3 mbar (1.5–2 Torr). All the depositions were performed on p-type Si(100) substrates (Okmetic Ltd.).

The optimal deposition temperature window was sought between 180 and 280 °C, where the lower and upper limits were defined by the TPA sublimation temperature and the too high desorption rate, respectively. In Fig. 2 (left figure) we plot the growth-per-cycle (GPC) values for films deposited at different temperatures as calculated from the film thicknesses (after 400 cycles) as determined by X-ray reflectivity (XRR; PANalytical model X'Pert PRO diffractometer, Cu K α radiation). The films had minor growth patterns when deposited at 180–200 °C and no patterns at 220 °C or higher temperatures. From the XRR data, the surface roughness was determined to be 7–8 nm (8 %) for films deposited at 180–195 °C, less than 1 nm (1 %) for those deposited at 200–240 °C, and 3–4 nm (2 %) at 260–280 °C. The notably higher surface roughness values for the films deposited in the lower temperature range already suggested that these films could be crystalline.

Most importantly, we used the XRR data to calculate the film densities as shown in Fig. 2 (left figure), where two sharp jumps are seen for the density value around the deposition temperatures of 195 and 260 °C. These jumps separate the three growth regions where in the low-temperature region the resultant film density is ca. 1.5 g/cm³, in the medium-temperature region ca. 2.1 g/cm³ and at the high temperatures higher than 2.8 g/cm³. The different film-density values could be explained by the formation of a porous MOF structure in the deposition temperature range of 180–195 °C, the growth of amorphous inorganic-organic hybrid films at 200–260 °C and the high desorption rate of the non-dense

organic molecules at temperatures higher than 260 °C. Note that the typical density of crystalline copper paddlewheel structures with alcohol molecule ligands has been reported to be 1.5±0.1 g/cm³.²⁸ Independent of the deposition temperature the films were found to grow in an essentially ideal ALD/MLD manner as far as the linearity is concerned, *i.e.* showing linear dependency of the film thickness (as determined by ellipsometry; Spectroscopic ellipsometer, SE 805) on the number of ALD/MLD cycles; in Fig. 2 (right figure) this is demonstrated for both the low-density Cu-TPA films deposited at 180 °C and the medium-density films deposited at 220 °C. Moreover confirmed was that the surface reactions are saturative, see the data for the GPC *versus*

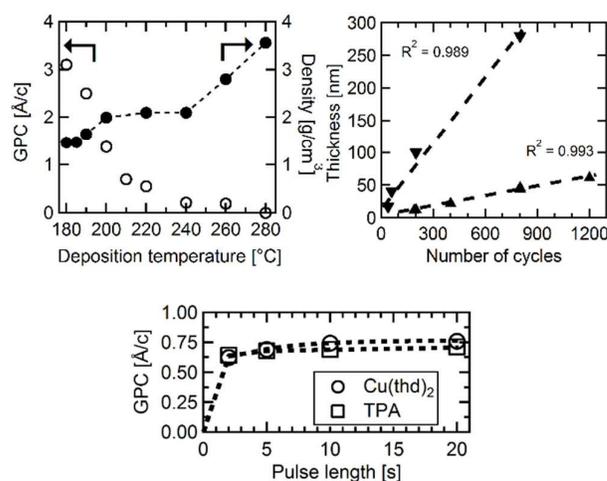


Figure 2. Left: Growth-per-cycle (o) and density (●) for our Cu-TPA films deposited at different temperatures. Right: Confirmation of the essentially linear film growth for the crystalline Cu-TPA (▼) and amorphous Cu-TPA (▲) films deposited at 180 and 220 °C,

respectively. *Bottom*: Confirmation of the saturation of the GPC value with increasing pulse lengths for both precursors, here at the deposition temperature of 210 °C.

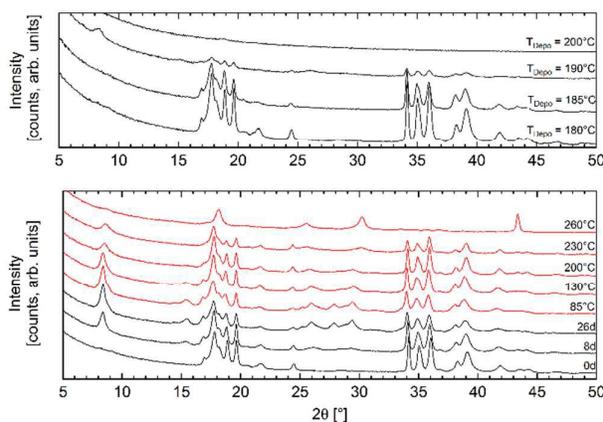


Figure 3. Top: X-ray diffraction patterns recorded for our as-deposited Cu-TPA films fabricated at different temperatures. Bottom: Patterns for the film as-deposited at 180 °C, then stored in open air for 26 days and finally annealed at different temperatures from 85 to 260 °C.

precursor pulse lengths in Fig. 2 (bottom figure), and that the pulse lengths as short as 5–10 s are enough to guarantee the essentially ideal ALD/MLD growth. For the further experiments we fixed the pulse and purge lengths as follows: 5 s Cu(thd)₂ / 2 s N₂ / 10 s TPA / 20 s N₂.

Our conclusions based on the XRR data for the film growth characteristics and crystallinity were then confirmed by grazing incidence X-ray diffraction (GIXRD; PANalytical model X'Pert PRO diffractometer, Cu K α radiation, $\lambda = 1.5405980$ Å, 0.5° angle) data displayed in Fig. 3 for our Cu-TPA films deposited at different temperatures (note that the film thickness for all the samples was 80–90 nm). Indeed, from GIXRD patterns for the as-deposited films (upper panel in Fig. 3) diffraction peaks are seen for films up to the deposition temperature of 195 °C with decreasing intensities with increasing deposition temperature. Most remarkably, the peaks perfectly fit to the paddlewheel-type MOF-2 structure, and similar patterns have been acquired from powder diffraction measurements for bulk copper terephthalate^{24,25} and copper cyclohexanedicarboxylate²³ MOF materials.

Preliminary information of the gas-storage capability of our Cu-TPA MOF films was obtained by observing their water absorption behaviour. Namely, it was found that upon an extended exposure to open (humid) air the crystalline Cu-TPA films of the MOF-2 structure absorbed moisture over time, seen as a gradual appearance of new diffraction peaks, see the lower panel in Fig. 3. The peaks typical for hydrous Cu-TPA structures arise after 8 days of air exposure, and are fully visible after 26 days. The paddlewheel structure is seen to sustain, indicating the water absorption to the free ligand spot in the structure.

The water absorption process was confirmed to be reversible, since after heating the sample in vacuum at 200 °C for 2 days, the peaks due to the hydrous structure were seen

to disappear nearly completely. During the water absorption the peaks broaden, indicating decreasing ordering of the structure presumably due to uneven distribution of H₂O molecules in the structure. The peaks moreover slightly shift to lower 2 θ angles (Fig. 4), indicating the expansion of the crystal lattice. During the

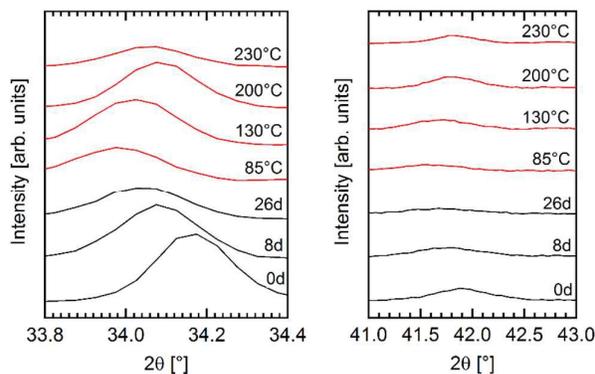


Figure 4. Parts of X-ray diffraction patterns for our Cu-TPA film deposited at 180 °C showing the gradual shifts of the peaks towards lower 2 θ values as the MOF structure absorbs moisture, and then returns to its original position when the moisture is excluded with heating in vacuum, as seen from (2 0 0) and (0 0 5) peaks at ca. 34.1° and 41.9°, respectively.

heating, the peaks again sharpen confirming the regeneration of the original structure until the structure is lost due to decomposition around 230 °C.

Finally we confirmed the presence of the organic ligand and its coordination to the copper atoms using Fourier transform infrared spectroscopy (FTIR; Nicolet, Magna-IR Spectrometer 750) and investigated the elemental composition of the films with X-ray photoelectron spectroscopy (XPS; Kratos Analytical). The FTIR spectra for our Cu-TPA films deposited at different temperatures are shown in Fig. 5. The coordination of carboxylate and metal species appears to be of the bridging type from the ν_{as} and ν_{s} , at ca. 1525 and 1390 cm⁻¹, respectively,²⁹ which is in good agreement with the paddle-wheel-type structure. Benzene ring shows characteristic peaks at ca. 1600, 1580, 1490 and 1440 cm⁻¹.³⁰ The FTIR data also confirm that the as-deposited films have neither coordinated H₂O nor –OH. The intensities of the spectral features diminish with increasing deposition temperature presumably due to the decreasing film thicknesses, as the number of deposition cycles (rather than the thickness) was fixed (at 400) for the films. The XPS spectra were collected for two Cu-TPA films, deposited at 180 and 210 °C. The theoretical C:Cu and O:Cu ratios for the MOF structure are 8:1 and 4:1, respectively, while the corresponding experimental values were 10.1:1 and 4.8:1 for the crystalline Cu-TPA deposited at 180 °C, and 14.4:1 and 6.6:1 for the amorphous Cu-TPA film deposited at 210 °C. In both cases the ratio for the carbon and oxygen excess is very close to 2:1, which is the C:O ratio in a terephthalate molecule. Hence the data apparently reveal that the surface of our films has excess of TPA molecules. This is natural as the depositions were

always finished with a TPA pulse. These are seen in the surface-sensitive XPS data but not in the bulk-sensitive FTIR data. Additionally, the XPS data unambiguously confirmed the divalent oxidation state for copper.

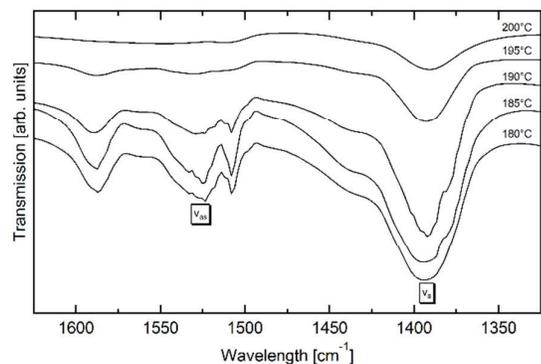


Figure 5. FTIR spectra for our Cu-TPA films deposited at different temperatures showing the bridging-type carboxylate coordination into copper atoms from the wavelength difference of symmetric and asymmetric vibrations of COO⁻ group.

In conclusion, we have demonstrated that crystalline thin films of the copper(II)terephthalate with the paddlewheel MOF-2 type structure can be deposited in an atomic/molecular layer-by-layer manner using the gas-phase ALD/MLD thin-film technique. Hence we now have a new industrially-feasible gas-phase technique to fabricate homogeneous and conformal MOF coatings in a highly-controlled way on various substrate surfaces or device architectures. Even though the temperature window of the MOF formation in this study was relatively narrow, i.e. 180–190 °C, optimizing the precursor and/or reactor design might help us in widening the temperature range for the successful ALD/MLD fabrication of crystalline films.

Then an interesting question concerns the choice of the precursors; we do positively foresee that our single-step ALD/MLD process could be extended to a number of other interesting metal-organic pairs to realize a fundamentally new family of layer-by-layer grown MOF coatings for future demands.

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