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Selective growth of MFU-4*l* single crystals on microstructured plasma polymer coatings†

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Single crystals of the metal–organic framework Ulm-4*l*(arge) (MFU-4*l*) can be grown site selectively on microtextured plasma polymer coatings comprising a pattern of alternating hydrophilic and hydrophobic domains. The crystals grow preferentially on the hydrophilic parts of the film surface. X-ray diffraction (XRD) shows that the cubic crystals have a high propensity to adhere with ⟨1 0 0⟩ orientation to the coating.

Plasma enhanced chemical vapor deposition, often referred to as plasma polymerization, is a fast and easily up-scalable process to produce highly cross-linked polymeric coatings from monomers, which are usually not amenable to controlled polymerization reactions. The chemical and physical properties of plasma coatings such as surface energy, chemical stability, and film thickness depend strongly on the chosen monomer(s) and on the polymerization conditions (*i.e.* pressure, power input, and duration) during the deposition process.[1,2] Their very high stability in particular should render plasma polymer films adjustable templates to direct and control the heteroepitactic growth of inorganic functional materials such as metal–organic frameworks (MOFs).

MOFs are porous, crystalline materials with very large internal surface areas.[3] Besides the commonly reported applications[4–6] MOFs are also suitable for chemical sensing devices for gases or vaporous molecules.[7] MOF thin films are commonly employed as chemically responsive layers, whereas the signal transduction is achieved through different approaches.[8] Until now a variety of MOFs[9–13] have been grown on different substrates. The first functional sensing device featuring a signal transduction from MOF to sensor has been reported by Allendorf *et al.* employing HKUST-1 grown on a self-assembled monolayer (SAM).[14]

This approach has been continued by other groups,[15–18] aiming either towards spatial discrimination or preferred orientation of MOF crystals. Recently a first report has demonstrated the utility of patterned plasma polymer coatings to produce a patterned layer of MOF crystals, in which the crystals, however, were lacking preferred orientation(s).[19] This contrasts the commonly observed highly oriented growth of MOF crystals on SAMs.[20]

Since plasma polymer coatings typically are chemical and physical robust entities, their usage as template matrices for MOF thin films seems highly promising, especially for those MOF compounds requiring harsh synthesis conditions incompatible with SAMs.[21,22] Moreover, plasma polymer coatings can be deposited on virtually any substrate in contrast to SAMs that often require well-defined precious metal surfaces.

The employed plasma system was previously described in detail.[23] After etching the glass substrates three subsequent layers of plasma coatings were deposited.

The first layer deposited consists of plasma polymerized hexamethyldisiloxane (ppHMDSO) serving as a coupling agent between the silica surface and the subsequent organic, hydrophilic coating of propionic acid (ppPA). *n*-Heptane was used as monomer for the last, polyethylene-like layer (ppH), thus, providing a hydrophobic surface.[1]

The plasma coatings were patterned *via* irradiation with ultra violet (UV) light through a quartz/chromium mask. The mask features transparent circles with a diameter of 20 μm.

UV lithographic etching resulted in hydrophilic, periodic, circle shaped cavities corresponding to the pattern of the mask.[24] For detailed Experimental data see ESI.†

In order to characterize the chemical changes introduced to the films by UV etching, X-ray photoelectron spectroscopy (XPS) was applied to model coatings before and after UV irradiation. XPS data indicate that irradiated coatings have a significantly higher amount of oxygen functions than non-irradiated films, as demonstrated by an increase of the O 1s peak integrated intensity compared to that of the C 1s peak of approximately 30%.

To demonstrate changes of the UV-etched film areas in terms of additional oxygen functions and surface charges, respectively, Auger spectroscopy was performed on patterned substrates

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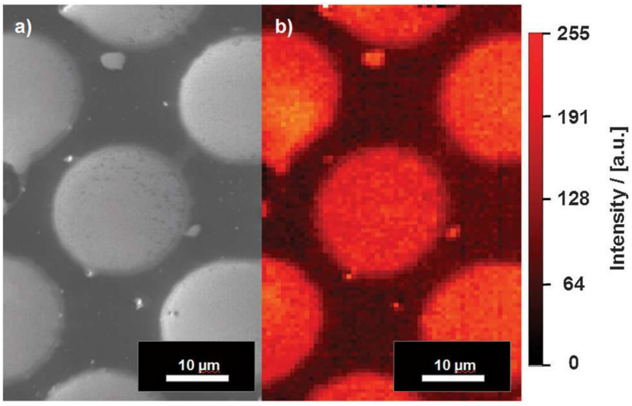

Fig. 1 (a) SEM micrograph and (b) Auger microscopy zinc mapping micrograph of identical areas of a UV-etched (90 min) multilayered plasma polymer coating deposited on a silicon substrate.

upon immersion of the latter into a solution of $ZnCl_2$. Spatially-resolved Auger spectra reveal a significant uptake of zinc ions by the hydrophilic surface areas.

Fig. 1a represents a SEM micrograph of a plasma coating exhibiting a circular pattern. The bright circles correspond to irradiated areas which are lower in height than non-irradiated (darker) areas. The step height measured with an atomic force microscope was approximately 70 nm.

A false colour background corrected zinc mapping of exactly the same area of the sample surface is shown in Fig. 1b. The brightness correlates to the amount of zinc detected. The edges of the zinc containing areas are very sharp and match exactly the corresponding regions shown in the SEM image.

To demonstrate the utility of micro-patterned plasma polymer coatings as a template for epitaxial overgrowing MOF crystals, patterned films were exposed to a typical mother liquor from solvothermal synthesis of MFU-4*l* crystals as previously described by our group.[25] Optical microscopy proved that the patterned multilayer coatings showed no signs of delamination or mechanical damage.

SEM micrographs show spatially defined, periodic circular-shaped areas of MFU-4*l* single crystals (see Fig. 2a and b), which have grown on the hydrophilic areas of the patterned films exclusively. The size distribution of the cubic MFU-4*l* crystals is quite narrow ranging from 500 nm to 1 µm for each crystal edge. A close up of the crystals (see Fig. 2c) indicates preferential ⟨1 0 0⟩ orientation.

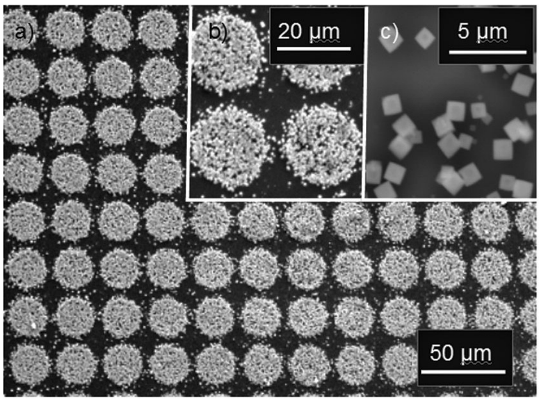

Fig. 2 (a and b) SEM micrographs of MFU-4*l* crystals grown on a micro-patterned plasma coating.[5] (c) SEM close-up of MFU-4*l* crystals grown on hydrophilic plasma coating.

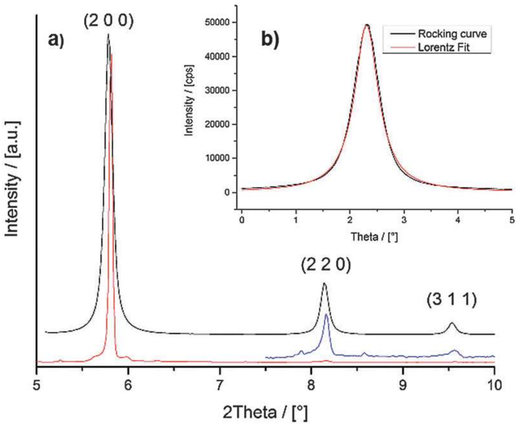

Fig. 3 Comparison of a measured powder pattern of MFU-4*l* grown on UV-irradiated plasma coated substrate (red) and of a simulated powder pattern (black). The blue line represents a selected area of the measured pattern magnified by a factor of 30. Inlet: Rocking curve of the (2 0 0) reflex of MFU-4*l*.

Since the crystals have no azimuthal orientation, the exact determination of crystal orientations *via* pole figure analysis is not possible. Instead, the intensities of three reflections of the measured powder pattern are compared to the corresponding three reflection intensities of a simulated powder pattern (*cf.* Fig. 3a).

The intensities of the (2 0 0), (2 2 0), and (3 1 1) reflections (2theta = 6.0°, 8.2°, and 9.6°) are chosen to calculate orientation distributions. Assuming that the simulated powder pattern represents the intensities of a statistical distribution of MFU-4*l* crystals, the three intensities of the simulated XRD pattern are normalized, to get a relative frequency of 33.3% for each orientation.

Using the same normalizing factor for the measured XRD pattern results in a relative frequency of 90% for the ⟨2 0 0⟩ and about 5% for the ⟨2 2 0⟩ and the ⟨3 1 1⟩ orientation, respectively, which is in good agreement with the representative orientations of crystal specimen as observed in SEM images.

As further proof of preferential crystal orientation of the MFU-4*l* crystals, the rocking curve of the reflex with the highest intensity was measured. The FWHM of the rocking curve is approximately 0.5°, which is about one order of magnitude higher than a FWHM of a single crystal measured using the same diffractometer set-up. However, the experimental rocking curve of MFU-4*l* crystals grown on the micro-patterned plasma polymer still differs significantly from a sample of randomly oriented crystals, which would not show a distinctive rocking curve at all.[26]

Fig. 4 represents a putative interface model of MFU-4*l* grown on a hydrophilic domain with ⟨1 0 0⟩ orientation. Linker molecules emanating from the surface of MFU-4*l* single crystals

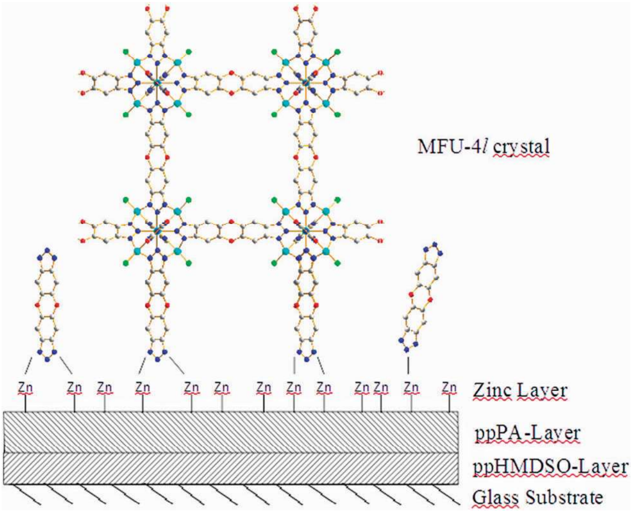

Fig. 4 Interface model showing the putative interactions between a MFU-4*l* crystal and the zinc ion adlayer formed on a hydrophilic domain of the plasma polymer thin film.

interact with the layer of zinc ions attached to the surface of hydrophilic domains, presumably *via* "free" nitrogen donor atoms from the triazolate linkers. Since plasmer polymer films generally are not expected to display any long-range structural order, the experimentally observed preferential growth orientation of MFU-4*l* crystals is not related to an epitaxial (*i.e.* geometric) match of the two juxtaposed surfaces. However, alternative concepts such as surface charge density matching[27] have been proposed for related model systems and future investigations encompassing a broader variety of plasma polymers thin films and MOF structural archetypes shall address this conceptionally and technologically interesting phenomenon.

In summary we show that it is possible to direct the growth of MOF crystals to the hydrophilic areas of a UV etched micropatterned plasma polymer coating. The MFU-4*l* crystals chosen as a model system grow with preferential ⟨1 0 0⟩ orientation. Results from scanning Auger microscopy indicate that the spatial selectivity of the crystals growth on top of the plasma polymer coating correlates with an enhanced concentration of zinc ions adhering to the hydrophilic domains of the micropatterned coatings. The surprisingly uniform orientation of the MOF crystals with respect to the film surface is an experimental observation, which is at odd with the common explanation of a heteroepitaxial match between metal coordination-active donor functions on the substrate's surface and the over-growing crystals, since plasma polymers are lacking any long-range structural order. Future investigations, therefore, will focus on elucidating the particular mechanism of crystal growth on these particular polymer films.

In light of the ease of preparation, the variability of monomers available and the enhanced chemical stability of the resulting plasma coatings the engineering of robust micro-patterned MOF thin films used in MOF sensors[28] or MOF microelectronic devices[29] seems to be a technologically attractive goal.

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