Spontaneous rearrangement of para-sexiphenyl crystallites into nano-fibers

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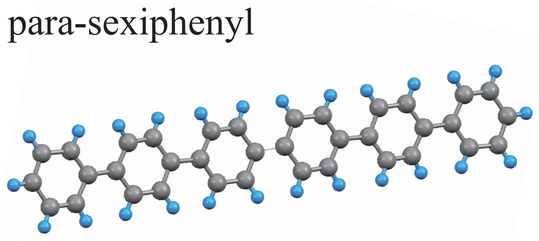
Motivation

Para-sexiphenyl (6P) is an organic, optical active semiconductor with potential for a variaty of applications. A high degree of control over the growth process is necessary to fabricate device quality layers.
Here, we report on an atomic force microscopy study on the spontaneous formation of high aspect ratio crystallite chains. The internal structure of these chains -- which is related to the crystallites formed during the intial growth stage -- could be revealed. A statistical analysis of the chain dimensions together with thermal desorption spectroscopy and x-ray data allows to explain the spontaneous formation process.

Experimental

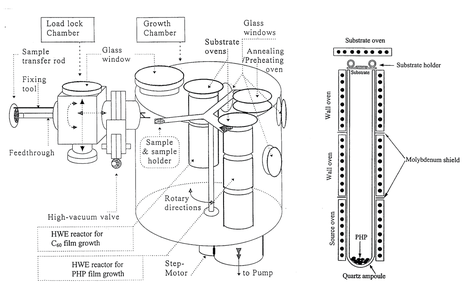
para-sexiphenyl



data
- monoclinic in $P2_{1/c}$ space group
- herringbone type bulk structure
- a = 0.809 nm, b = 0.557 nm, c = 2.624 nm, ß = 98.17°
* molecule length: 26.3 Å
* molecule width: 4.3 Å

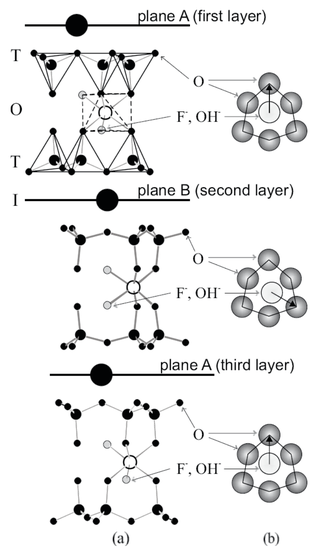
Hot Wall Epitaxy

Deposition temperature: 90°C
Base pressure: $1x10^{-6}$ mbar
Source temperature: 240°C
Wall temperature: 260°C
Deposition rate: ~2 nm/min

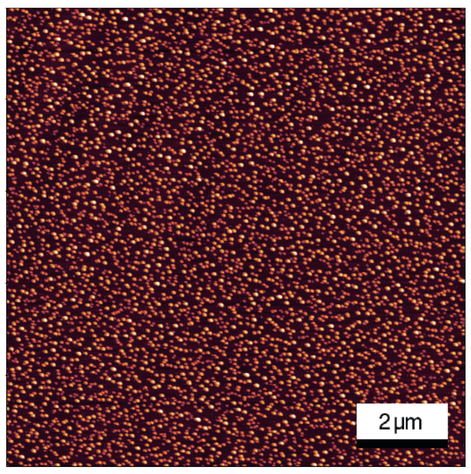


mica(001)

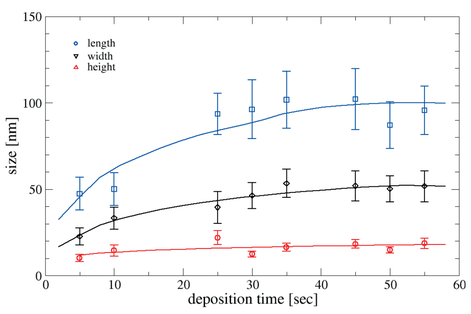
The mica(001) surface used is a cleavage plane of $2M_1$-muscovite with the formula $KAl_2(AlSi_3)O_{10}(OH,F)_2$. Due to charge repulsion between the oxygen in the top most layer the anions are displaced from the center of the hexagonal opening - which leads to a twofold symmetry of mica(001).



Early growth stage



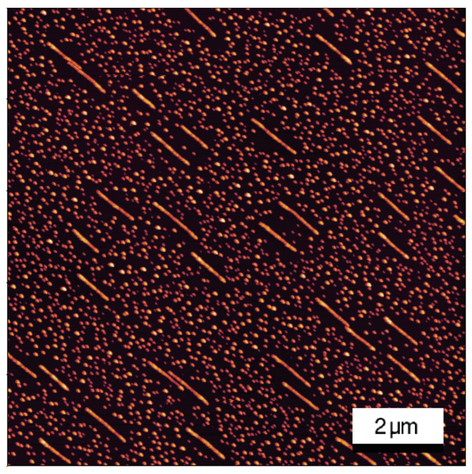
6P crystallites on mica(001) after 30 sec of deposition. w=50 nm, l=100 nm, and h=10 nm.



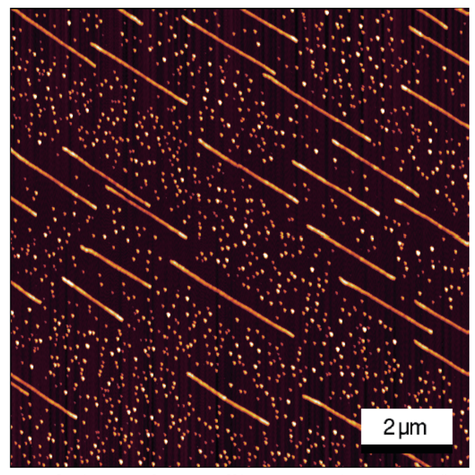
Evolution of crystallite size with ongoing deposition.

Crystallites of uniform size are formed during the first 30 s of deposition.

Intermediate growth stage



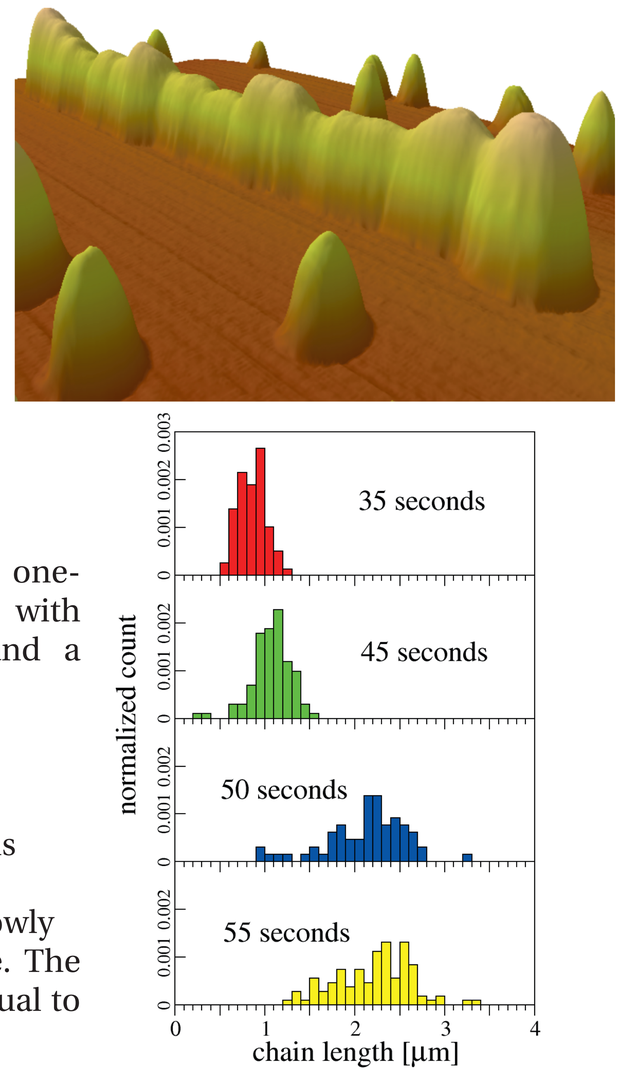
6P chains and crystallites on mica(001) after 45 s of deposition. Chain length 1µm.



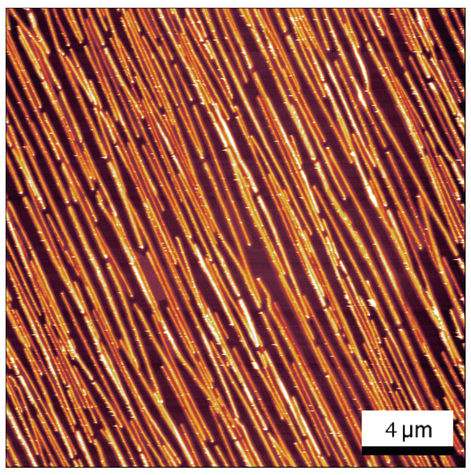
6P chains and crystallites on mica(001) after 55 s of deposition. Chain length > 2 µm.

Formation of parallel, one-dimensional chains after 35 s with uniform length distribution and a threshold length
With ongoing deposition:
- Av. chain length increases
- Min. chain length increases
- Length distribution broadens due to coalescence
- Width and height change slowly

Chains have internal structure. The size of the chain segments is equal to the size of the crystallites.

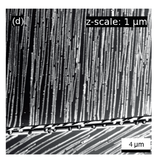


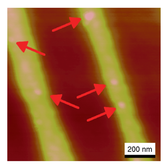
Final growth stage



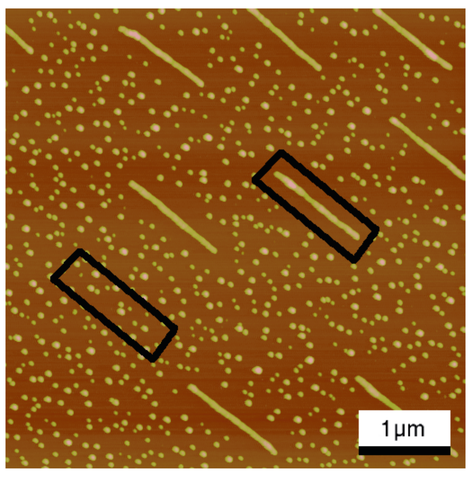
6P chains and crystallites on mica(001) after 55 s of deposition. Chain length > 2 µm.

No crystallites on the mica surface, but the whole surface is covered by parallel running large aspect ratio chains.
Two 120° rotated domains exist due to the alignment of the 6P with mica(001) dipols.
More crystallites can be found on top of existing chains.

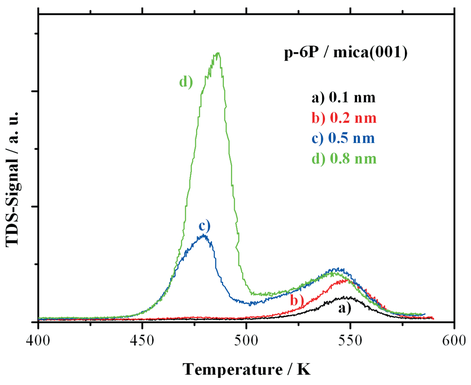




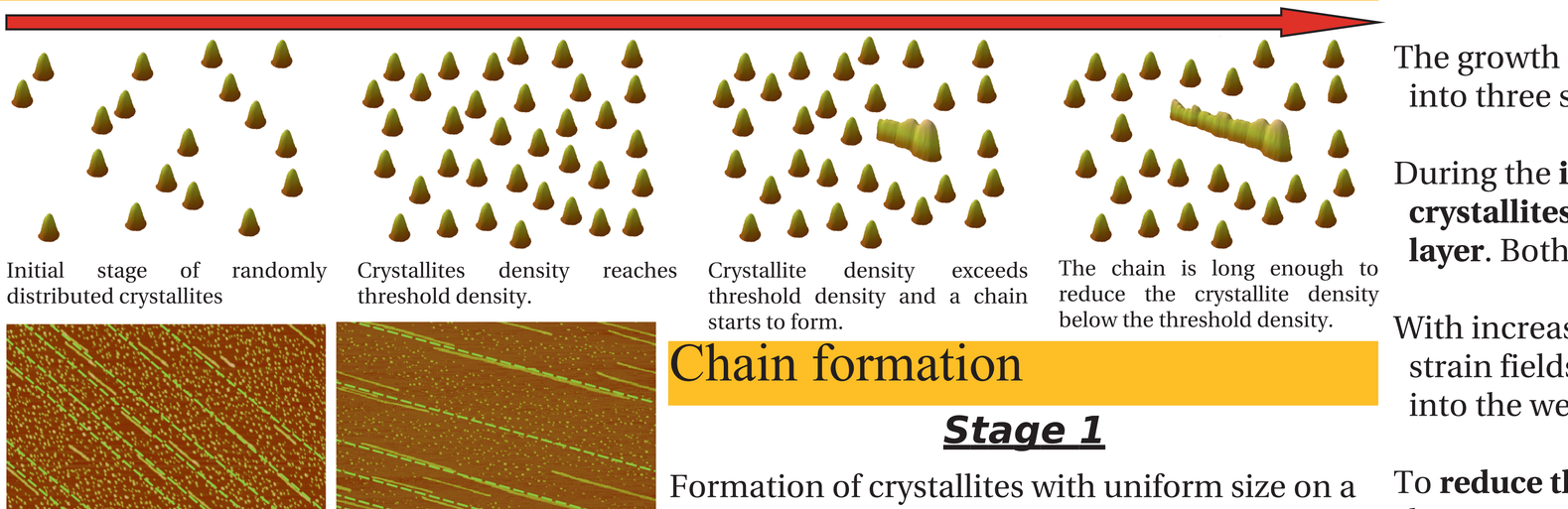
Growth scenario



A denuded zone exists around the chains which is free of crystallites. The lower rectangle holds sufficient crystallites to form a chain with the same length as in the upper rectangle.



Thermal desorption spectra of 6P on mica(001) for different film thickness. The monolayer peak at 550 K saturates around 0.5 nm film thickness. This corresponds to a single layer of lying molecules.



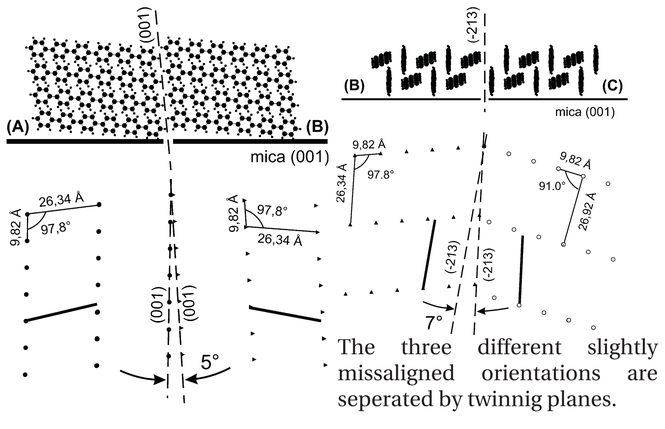
Initial stage of randomly distributed crystallites

Crystallites density reaches threshold density.

Crystallite density exceeds threshold density and a chain starts to form.

The chain is long enough to reduce the crystallite density below the threshold density.

(a) 6P chains as grown. The green dashed lines indicate the position of the proposed defects in the wetting layer. (b) After annealing the chain length has increased. New chains are only formed where a defect exists but no new defects are formed.



The three different slightly missaligned orientations are seperated by twinnig planes.

Chain formation

Stage 1

Formation of crystallites with uniform size on a wetting layer of lying molecules.

Stage 2

Above a critical density the crystallites regroup as entites using defects in the wetting layer as seeds. This reduces the stress in the wetting layer -> new crystallites can form.

Stage 3

The whole surface is covered by chains.

Summary

The growth of 6P on mica(001) can be split into three stages:

During the **intial growth stage** small **crystallites** are formed **on** top of **a wetting layer**. Both are formed of lying molecules.

With increasing crystallite density the strain fields induced by the crystallites into the wetting layer start to overlap.

To **reduce the strain**, defects in the wetting layer act as **seeds for the formation** of **crystallite chains**.

The formed chains are oriented with respect to the mica(001) surface and have a **narrow length distribution**.

This chains are formed by crystallites -- which roughly contain 140000 mocules -- as entities.

References

Teichert, C. et al., Appl. Phys. A 82, 665-669 (2006)
Plank, H., et al., Thin Solid Films 443, 108-114 (2003)
Frank, P., et al., Surf. Sci. 601, 2152-2160 (2007)

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