# INTERMEDIATE PHASES OF PYROLYTIC CARBON OBSERVED BY ATOMIC FORCE MICROSCOPY

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## Introduction

Two deposition mechanisms were postulated for the chemical vapor deposition of pyrolytic carbon [1, 2]: chemisorption of small hydrocarbon species at active sites of the substrate surface (denoted as *growth mechanism* by Hüttinger et al. [1]) and physisorption of planar polyaromatic species on basal planes (denoted as *nucleation mechanism*). Whereas Bourrat et al. report the deposition of smooth laminar carbon by chemisorption and of rough laminar carbon by physisorption [2], Hüttinger et al. emphasize that the deposition mechanism does not directly determine the degree of texture [3]. For the nucleation mechanism, i.e. the physisorption of planar molecules, Hüttinger's model predicts an intermediate phase of pyrolytic carbon where the polycyclic hydrocarbon can still align and reorient after deposition. So far, a direct observation of this intermediate phase has not been reported.

In this paper we present the direct experimental observation of an intermediate phase of pyrolytic carbon by a combination of atomic force microscopy techniques in the regime where deposition in the nucleation mechanism is predicted according to Hüttinger's model.

## Experimental

*Sample Synthesis*
Pyrolytic carbon films were deposited in a hot wall reactor at a temperature of 1100 °C from pure methane. Three different types of channel structures consisting of cordierite ($Mg_2Al_4Si_5O_{18}$) were used as substrates: S25 with a ratio of surface area to free volume A/V of 0.79 $mm^{-1}$, S100 (A/V 1.56 $mm^{-1}$) and S400 (A/V 3.22 $mm^{-1}$). Pyrolytic carbon films deposited at methane partial pressures between 4 kPa and 50 kPa were investigated. The gas flow was adjusted to reach a maximum residence time $\tau$ of 1 s at the end of the cordierite substrate. Samples were cut from the top (residence time 0.875 s) and the bottom (residence time 0.125 s) of the channel structure. Details of the deposition process are described elsewhere [4, 5]. The thickness of the carbon films was between 50 µm and 200 µm. The texture of the pyrolytic carbon films was investigated by polarized light microscopy [6] and by selected area electron diffraction by Hu et al. [7]. The sample surfaces were investigated by atomic force microscopy and lateral force microscopy without any further treatment.
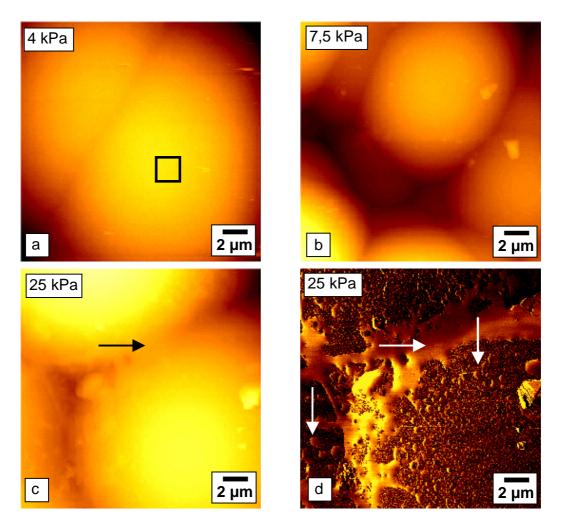
Figure 1: Pyrolytic carbon layers on cordierite: Influence of methane pressure. The horizontal arrows in c) and d) mark smooth structures in trenches between adjacent hillocks. Substrate S25, residence time 0.125 s, scan area 20 µm x 20 µm, a), b), c) AFM topography, a) $p_{methane}$ = 4 kPa, z-scale 1 µm, b) $p_{methane}$ = 7.5 kPa, z-scale 2 µm, c), d) $p_{methane}$ = 25 kPa, z-scale 3 µm, d) lateral force microscopy.

**Results and Discussion**

Figures 1a, b and c show the AFM topography of surfaces of pyrolytic carbon films that were deposited at different methane pressures on cordierite. Apart from the methane pressure, the deposition parameters were kept constant for all four samples.

Hillocks with typical diameters of a few 10 µm and heights of a few µm are visible (average diameters are given in Fig. 2). Each of these hillocks corresponds to a growth cone nucleated at the substrate surface [8]. The surface of the hillocks consists of an

island film with typical average diameters of the islands of 100 nm which is well in the range of about 50 nm to 200 nm expected for pyrolytic carbon surfaces [8].

For methane pressures of 25 kPa and 50 kPa in the trenches between the hillocks additional structures are visible (see horizontal arrows in Fig. 1c and d). These structures can be identified clearly in the friction force microscopy image of Fig. 1d which was taken simultaneously with the AFM topography of Fig. 1c. The structures show a higher friction as compared to the rest of the pyrolytic carbon film. Additionally these structures show smaller variations of the friction force than the surrounding region, i.e. they appear smoother in the friction force image. On top of the hillocks the friction force image exhibits a roughness arising from the granular structure of the pyrolytic carbon surface. In addition to the connected smooth structures in the trenches between hillocks, smooth isolated islands can be observed on top of the hillocks (e.g. vertical arrows in Fig. 1d) that also exhibit an increased friction force.

During the deposition process, the surface related deposition rates and the gas composition were determined [4, 5, 7]. Fig. 2 shows the deposition rates in dependence on the deposition parameters determined by Hu et al. ($\Lambda$, ■ and ▲ give the measured data. The black line is a fit of the data according to Hüttinger's model [1]).

The circles correspond to AFM measurements: the filled circles indicate the observation of smooth structures that exhibit higher friction as compared to the surrounding pyrolytic carbon film. Open circles indicate no observation of such structures. The average diameter of the hillocks is given by the lengths printed close to the corresponding circles in Fig. 2. No monotonous dependence of the average diameter on methane pressure or surface area / volume ration was found, but for a residence time of 0.875 s the hillocks were larger than for a residence time of 0.125 s.

The measured dependence of the deposition rate on the methane pressure can be interpreted according to the model suggested by Hüttinger [1]: for smaller methane pressures pyrolytic carbon is deposited at active sites according to the growth mechanism. In this regime, the deposition rate increases until all active sites are saturated and thus adsorption saturation is reached. For higher methane pressures, according to Hüttinger's model deposition due to the nucleation mechanism occurs. This leads to an increase in the deposition rate.

Assuming that this interpretation is correct, Fig. 2 shows that for deposition in the nucleation mechanism the smooth structures discussed above are always found. Taking into account that the onset of the nucleation mechanism does not have to be abrupt and that the onset can only be estimated from the data of deposition rates, the occurrence of smooth structures can be understood as an attribute of deposition in the nucleation mechanism. The occurrence of an intermediate phase of pyrolytic carbon directly after deposition in the nucleation mechanism was predicted [1] and this intermediate phase can now be identified as the smooth structures discussed above.
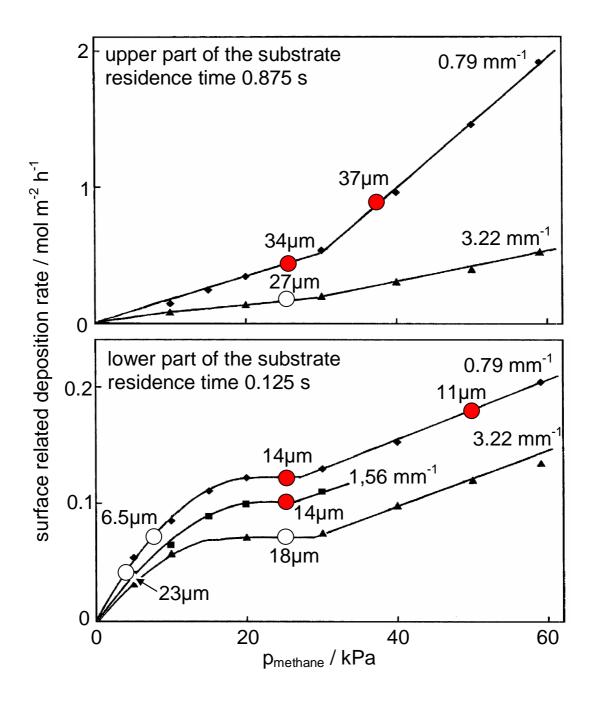
Figure 2: AFM results in comparison with the deposition rate vs. methane pressure (taken from [7]). ∧, ■ and ▲ give deposition rates for three different surface area / volume ratios. The circles correspond to samples that were investigated by AFM: the filled circles indicate samples where intermediate phases of pyrocarbon were found, whereas the open circles correspond to samples, where intermediate phases could not be observed. The average diameter of the hillocks is given for each sample investigated by AFM by the length printed close to the corresponding circle.

## Conclusions

Pyrolytic carbon layers deposited on planar cordierite substrates from methane were studied by atomic force microscopy and friction force microscopy. The pyrolytic carbon layers consist of growth cones that appear at the surface of the pyrocarbon layer as hillocks with typical diameters between 5 µm and 50 µm. The surface of these hillocks shows a granular structure with a typical grain size of 100 nm.

Under deposition conditions where deposition in the nucleation mechanism is expected, smooth structures at typical length scales between 100 nm and 5 µm were found on top of the hillocks. The observation of these smooth structures only under certain deposition conditions may be interpreted as indication for the existence of two deposition mechanism. Finally, the observation of the smooth structures which are clearly distinguishable by their higher friction from the rest of the pyrocarbon surface is the first direct experimental evidence for the existence of an intermediate phase of carbon as predicted for deposition in the nucleation mechanism by Hüttinger's model.

## Acknowledgements

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