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Direct observation of intermediate phases of pyrolytic carbon by atomic force microscopy

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Abstract

Pyrolytic carbon was deposited on planar substrates in a hot-wall reactor. A material contrast between silicon substrate and individual carbon islands was achieved by scanning force microscopy-based methods revealing two types of islands by different chemical contrast. This observation can be interpreted in terms of an intermediate phase of pyrolytic carbon according to a model by Hüttinger et al. [1]: for deposition in a regime where the nucleation mechanism dominates, an intermediate phase of pyrolytic carbon is predicted which is expected to have deviating mechanical properties. This agrees with our results of island removal experiments carried out using atomic force microscopy where defined lateral forces are applied to the islands: two types of carbon islands are found that differ significantly in the shear stress necessary for island removal.

Additionally, complete pyrolytic carbon layers were deposited on cordierite channel structures at methane pressures between 4 kPa and 50 kPa and residence times up to 1 s. Atomic force microscopy of these layers shows hillocks with typical diameters between 5 µm and 50 µm. At sufficiently high methane pressures where adsorption saturation is reached [2], additional carbon structures exhibiting different chemical contrast at typical length scales between 100 nm and 5 µm were found additionally on top of the hillocks. This observation is a direct experimental evidence for the existence of an intermediate phase of carbon as postulated for deposition in the nucleation mechanism.

Keywords: Pyrolytic carbon, atomic force microscopy, chemical vapor deposition

1. Introduction

According to Hüttinger et al. two deposition mechanisms can be distinguished for the chemical vapor deposition of pyrolytic carbon: a growth mechanism, controlled by chemisorption of small hydrocarbon species at active sites of the substrate surface, and a nucleation mechanism, corresponding to physisorption or condensation of polycyclic aromatic hydrocarbon species at the basal planes, respectively [1]. For the nucleation mechanism, i.e. the physisorption of polycyclic aromatic hydrocarbon species, an intermediate phase of pyrolytic carbon is postulated in which physisorbed or condensed polycyclic aromatic hydrocarbon species are able to align and reorient before carbon is formed by aromatic condensation reactions of the species [1]. So far, however, a direct observation of this intermediate phase has not been reported.

2. Experimental

2.1. Sample Synthesis

Pyrolytic carbon was deposited from methane on planar p-doped (100) silicon substrates with a native oxide in a hot-wall reactor at a temperature of 1100°C. The surface area / volume ratio was 0.26 mm^{-1}. Methane / argon mixtures at a total pressure of 100 kPa were used.

Additionally, pyrolytic carbon layers were deposited from pure methane at pressures from 4 kPa to 50 kPa on channel structures consisting of cordierite ($Mg_2Al_4Si_5O_{18}$). The residence time τ of the gas for the flow through the channel structure was 1 s. At the end of the deposition process the methane flow was turned off simultaneously with the heating system. The deposition of pyrolytic carbon stopped within a few seconds, because possibly still existing hydrocarbons in the gas phase are flushed away.

2.2. Atomic Force Microscopy (AFM)

AFM and FMM (force modulation microscopy) investigations were performed at ambient conditions using commercially available V-shaped silicon and silicon nitride cantilevers with force constants between 0.01 N/m and 0.25 N/m. The images were taken in the contact mode of the AFM in the repulsive force regime at a total normal force in the range of $0.1 – 0.6 \cdot 10^{-7}$ N.

3. Results and discussion

Force modulation microscopy was applied to achieve a material contrast between silicon substrate and carbon islands. Individual carbon islands were identified on the silicon substrate. Additionally, it was found that the islands exhibit different contrast indicating different mechanical properties.

In a further step, defined lateral forces were applied leading to the removal of part of the islands (see Fig. 1): a

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large number of islands was removed during the first ten scans whereas a few stable islands could not be removed. A correlation between removal rate and contrast in FMM was found. This could be interpreted in terms of an observation of different stages of a healing or reorientation process of an intermediate phase of pyrolytic carbon.

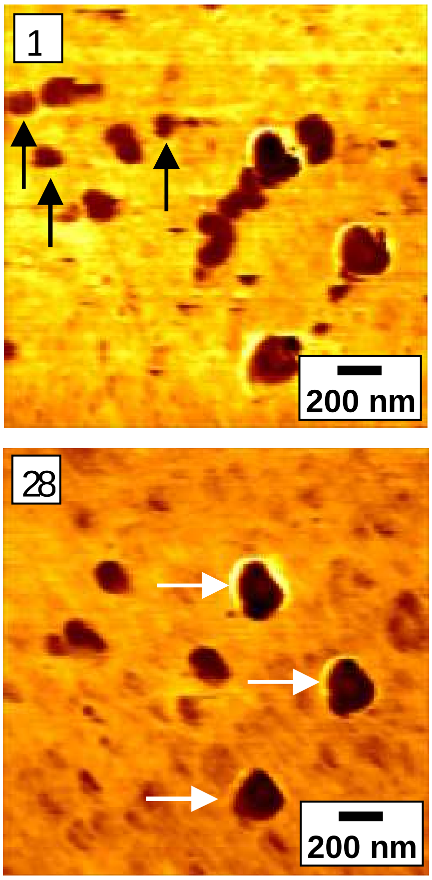

Fig. 1. Removal of carbon islands from a silicon substrate with the tip of an AFM. Two images of the same area taken by force modulation microscopy (scan number 1 and 28). Deposition time 90 min, residence time 0.05 s. Black arrows: islands that are not visible in scan number 2, i.e. these islands were easily removed. White arrows: stable islands that could not be removed under the chosen conditions.

Fig. 2 shows AFM images of a pyrocarbon layer deposited on cordierite: Hillocks with typical diameters of a few 10 µm were also observed. On top of these hillocks almost circular islands with typical diameters between 50 nm and a few 100 nm were found. The islands have a smooth surface and exhibit a higher friction coefficient than the surrounding surface.

These additional structures are only found under deposition conditions at which saturation adsorption is reached (compare [2]). This is in agreement with the regime predicted by Hüttinger [1] for the occurrence of an intermediate phase of pyrolytic carbon.

4. Conclusions

The AFM investigation of the early stages of the deposition of pyrolytic carbon revealed the existence of carbon islands with different mechanical properties. This can understood as the result of a healing process of an intermediate phase of pyrolytic carbon.

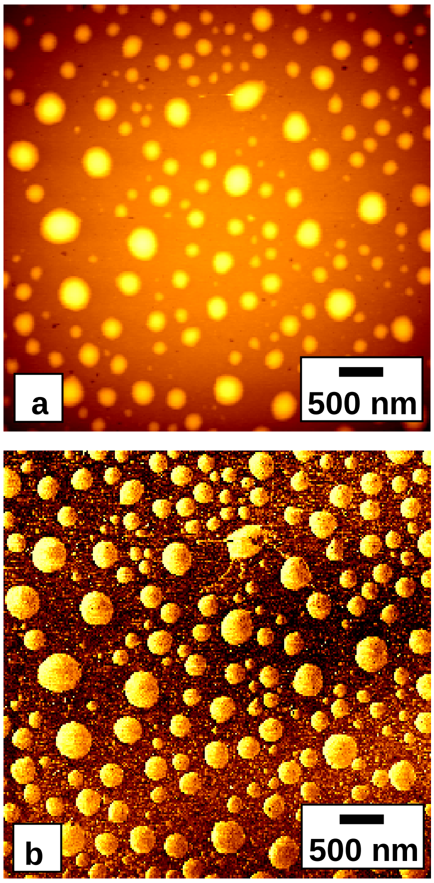

Fig. 2. Additional structures in a pyrocarbon layer on cordierite at a residence time of 0.875 s. $p_{methane}$ = 25 kPa, a) AFM topography, scan area 5 µm x 5 µm, z-scale 121 nm, b) friction force microscopy of the same area as in a), higher friction forces were observed in brighter areas.

Additionally, the surface morphology and properties of pyrolytic carbon layers deposited on planar cordierite substrates were studied atomic force microscopy and friction force microscopy. Under deposition conditions at which saturation adsorption is reached, additional structures, which are clearly distinguishable by friction force microscopy from the rest of the pyrocarbon surface, were found on top of the hillocks. These additional structures represent *the first direct experimental evidence for the existence of an intermediate phase of carbon* as postulated for deposition via the nucleation mechanism by Hüttinger et al. Additionally, the observation of the intermediate phase shows that Hüttinger's model is applicable within the considered regime of deposition parameters and that two different regimes of deposition exist. Therefore the observation of additional structures may also be interpreted as indication for the existence of two deposition mechanisms.

References

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