EARLY STAGES OF THE CHEMICAL VAPOR DEPOSITION OF PYROLYTIC CARBON INVESTIGATED BY ATOMIC FORCE MICROSCOPY

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Introduction

Pyrolytic carbon is deposited on carbon fiber felts to produce carbon / carbon composites. These composites combine high strength with low weight and a good temperature stability. Because of these properties carbon / carbon composites are used in high performance applications, e.g. aircraft brake assemblies or structural components in aerospace. The interface between carbon fibers and surrounding pyrolytic carbon is crucial for the macroscopic properties of the composite and it has been shown that, depending on the deposition parameters, the properties of the substrate surface can influence the deposition process on the µm-scale [1]. Therefore the initial stages of the deposition of pyrolytic carbon are of great technological interest.

In addition, the process of chemical vapor deposition of pyrolytic carbon has been described only qualitatively by different models and has not been understood in detail so far. The investigation of the initial stages of pyrolytic carbon deposition can give important insight into the deposition mechanisms and the correlation between the deposition parameters and the degree of texture of the resulting carbon material.

In this paper we demonstrate the identification of single carbon islands by force modulation microscopy. Three different nucleation mechanisms could be distinguished. With increasing residence time, a transition from single carbon islands to a complete carbon film is observed.

Experimental

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. Silicon was chosen to allow the identification of pyrolytic carbon against the substrate. The substrate was oriented parallel to the gas flow. The surface area / reactor volume ratio was 0.26 mm^{-1}. Methane / argon mixtures at a total pressure of 100 kPa were used.

One sample with a deposition time of 5 min and one sample with a deposition time of 90 min were selected for presentation in this paper (deposition parameters see Table 1).

Sample	$p_{methane}$	p_{argon}	Residence time τ_{end}	Deposition time t
Si223	20 kPa	80 kPa	3.2 s	5 min
P15	10 kPa	90 kPa	2.0 s	90 min

Table 1: Deposition of pyrolytic carbon on silicon: deposition parameters of the samples presented in this paper. τ_{end} is the residence time at the end of the reactor, i.e. near the gas outlet.

Results and Discussion

Fig. 1a shows the AFM topography of carbon islands deposited on a silicon substrate. Force modulation microscopy (FMM) was used to discriminate the carbon islands from substrate inhomogeneities and contaminations. Fig. 1b shows the FMM image that was acquired simultaneously with the AFM topography of Fig. 1a.

AFM topography shows a flat substrate with a root mean square (RMS) roughness of 2 nm. On top of the substrate two types of hillocks are observed:

- Carbon islands with diameters between 50 nm and 150 nm and heights between 8 nm and 15 nm that appear dark in the FMM images.
- Non-carbon islands, that exhibit no or no clear contrast relative to the substrate in FMM (e.g. islands marked by black squares in Fig. 1). These islands have typical diameters between 100 nm and 400 nm and heights between 10 nm and 20 nm.

For each of the carbon island, the FMM signal is nearly constant on the whole island, which suggests that the contrast in FMM is not influenced by the topography of the islands.

The identification of pyrolytic carbon by force modulation microscopy allows the investigation of nucleation mechanisms for the initial stages of deposition. Three nucleation mechanisms could be identified:

- Nucleation of single carbon islands randomly distributed on the substrate surface (Fig. 1a and b).
- Nucleation of islands along lines as shown in Fig. 1c.
- Nucleation of new islands at the edges of already existing islands (Fig. 1d), which will be denoted in the following as ’secondary nucleation’.

Nucleation along lines as shown in Fig. 1c is observed frequently. Once nucleated, the islands mostly do not grow along the lines, but almost spherically around the center of nucleation. The density of the decorated lines strongly depends on the location on the

sample. This decoration of lines is probably due to line defects which are possibly fine micro grooves resulting from the substrate preparation procedure.

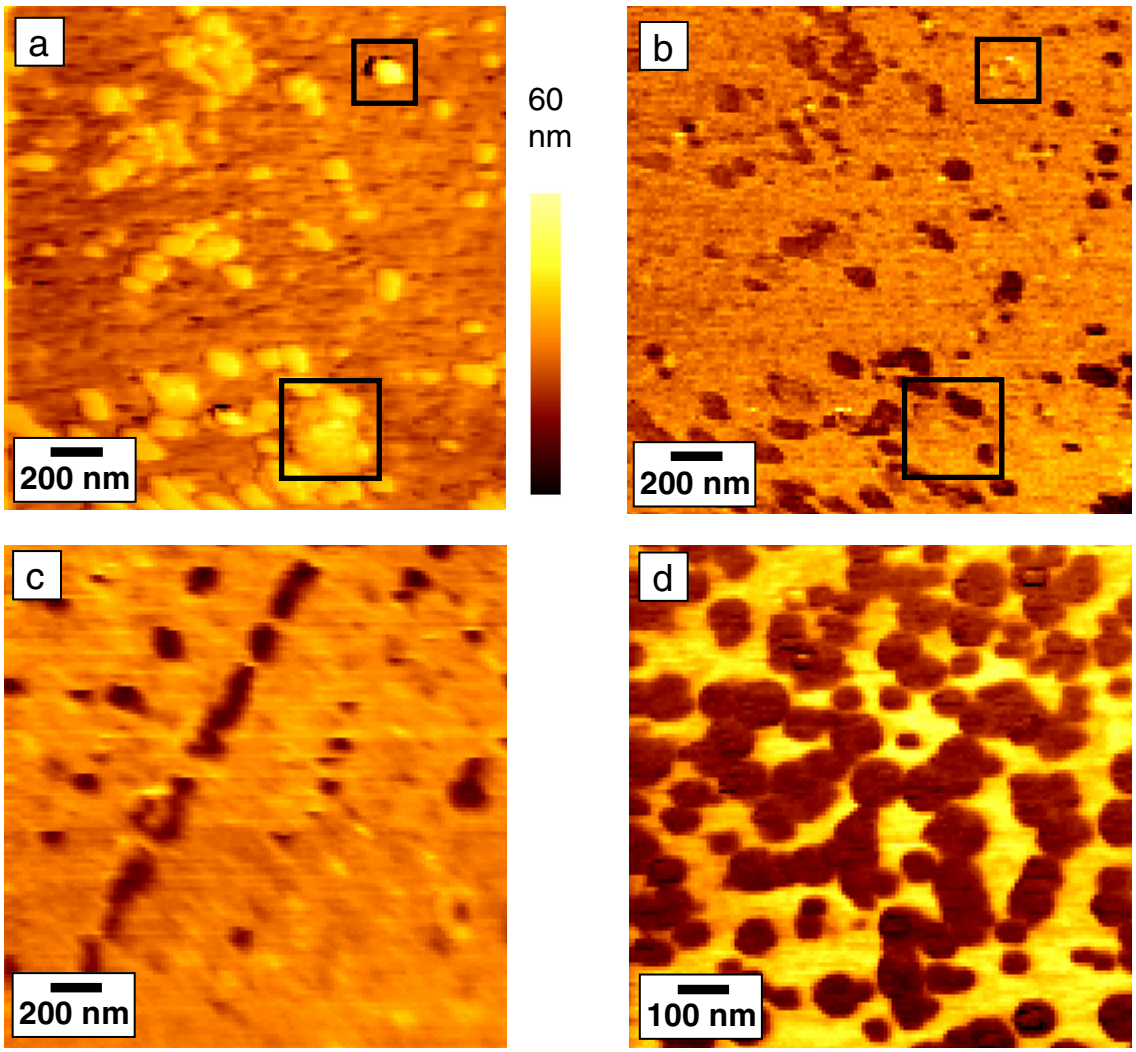

Figure 1: Identification of pyrolytic carbon islands on silicon by force modulation microscopy and observation of three nucleation mechanisms. a), b) Randomly distributed carbon islands, scan area 2 µm x 2 µm (sample P15, residence time 0.05 s), a) AFM topography, b) force modulation microscopy (modulation frequency 1.5 kHz, modulation amplitude 5 nm). The black squares mark non-carbon islands that do not appear dark in force modulation microscopy. c) Line nucleation, scan area 2 µm x 2 µm (sample P15, residence time 0.05 s, modulation frequency 1 kHz, modulation amplitude 10 nm), d) secondary nucleation, scan area 1 µm x 1 µm (sample Si223, residence time 1.34 s, modulation frequency 1.5 kHz, modulation amplitude 6 nm).

Finally, Fig. 1d shows agglomerates of carbon islands typical for higher degrees of coverage. Islands nucleate preferentially at the edges of already existing islands for the

case that all nucleation centers of the bare substrate are already covered by islands. This secondary nucleation leads to the observation of agglomerates of islands.

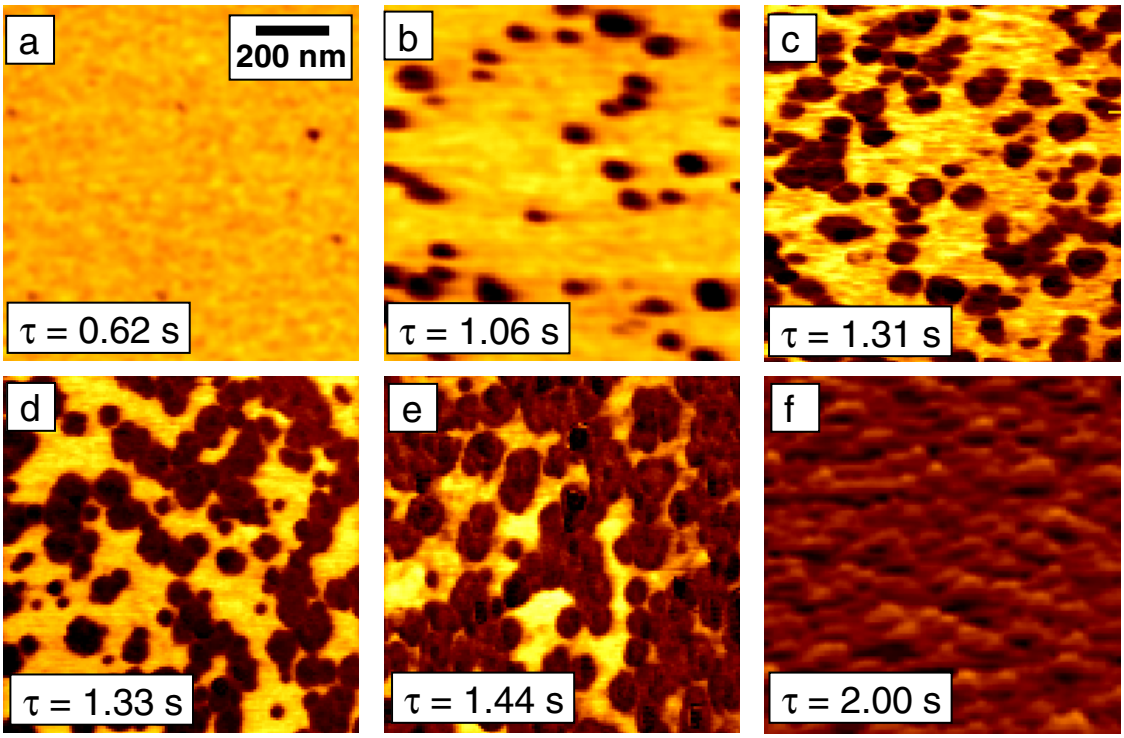

Figure 2: Transition from single islands to a complete carbon film: pyrolytic carbon deposited on silicon. Force modulation microscopy, scan area 1 µm x 1 µm, sample Si223, residence times τ are given in the images, modulation amplitude 6 nm, modulation frequency 1.5 kHz – 2.5 kHz.

Fig. 2 shows FMM images of different locations on the same sample. For a residence time of 0.62 s single carbon islands with diameters between 30 nm and 50 nm are visible as dark areas. The island density increases with residence time: first more and more islands become connected (Fig. 2e) and finally a complete carbon film is observed (Fig. 2f). The maximum diameter of the islands increases with residence time up to a value of about 80 nm to 100 nm reached for a residence time of 1.06 s (Fig. 2b). For higher residence times, the maximum diameter stays nearly constant. The degree of coverage also increases with residence time: for residence times below 0.95 s it is below 2 %, above 1.75 s a complete carbon film is observed. For the chosen deposition time of 5 min, the transition from only a few islands (degree of coverage below 2 %) to a complete carbon film occurs within a change of residence time of 0.8 s.

These results confirm the importance of the residence time for the deposition process and show that the deposition rate increases with residence time for the chosen deposition parameters. This trend is in accordance with the increase of thicknesses of pyrolytic carbon layers as a function of residence time determined by De Pauw et al. [2].

The investigations of the initial stages of pyrolytic carbon deposition give a maximum island diameter that is comparable with island diameters observed on the surfaces of complete films with thicknesses up to a few 100 µm. This might indicate that the mechanism of secondary nucleation is determining the island diameter. Once the substrate is completely covered, under appropriate conditions the secondary nucleation is independent of the substrate surface structure and should lead to similar carbon films for different substrates. On the other hand, it has been shown that the substrate can influence the structure of a pyrolytic carbon film well beyond the vicinity of the substrate pyrolytic carbon interface under certain conditions [1].

Conclusions

Pyrolytic carbon was deposited on planar silicon substrates from methane in a hot-wall reactor. At short residence times single pyrolytic carbon islands were identified on the silicon substrate using force modulation microscopy.

Three different nucleation mechanisms were found: random nucleation of single islands, nucleation of carbon islands along lines and secondary nucleation which corresponds to the nucleation of carbon islands at edges of already existing carbon islands.

The transition from individual carbon islands to a complete carbon film was observed with increasing residence time. This is in agreement with the observation that with increasing residence time, the pyrocarbon deposition rate is increasing. Similar sizes are observed for individual islands close to this transition from separate islands to a complete film and for the grain structure of thicker carbon films, suggesting a strong influence of secondary nucleation on the dimensions of carbon islands.

References

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