

## EARLY STAGES OF PYROCARBON DEPOSITION ON PLANE SUBSTRATES IN A HOT WALL REACTOR

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### Introduction

The understanding of the correlation between the deposition parameters and the pyrocarbon structure - in particular the texture - is important to control e.g. the mechanical properties of carbon fiber / carbon matrix composites. The particular aim of the present work was the study of the initial stages of the pyrocarbon deposition. For this purpose, pyrocarbon was grown on silicon wafers in a hot-wall reactor by chemical vapour deposition (CVD). Thickness profiles and the texture of the pyrocarbon were measured as a function of the residence time by scanning and transmission electron microscopy (SEM, TEM). The surface topography was studied by atomic force microscopy (AFM).

### Experimental Techniques

The pyrocarbon was deposited in a hot-wall reactor from a 10 % methane / 90 % argon mixture at a total pressure of 100 kPa and a temperature of 1100°C. The silicon substrate was oriented parallel to the gas flow. The residence time  $\tau$  of the gas increases along the substrate and reaches 2 s at the end of the reactor. The influence of oxygen on the pyrocarbon texture was investigated by using an O<sub>2</sub>/Ar mixture as diluent gas, with overall O<sub>2</sub> concentrations of 0, 0.1, 1 and 3 %. The thickness of the carbon layers can be considered as a direct measure of the deposition rates because the deposition time was always 1 h.

The TEM was carried out using a Philips CM 200 FEG/ST electron microscope. The texture is evaluated from selected area diffraction patterns by measuring the orientation angle (OA), which corresponds to the FWHM intensity of the azimuthal opening of the arc of (002) reflections, similar to the technique published by Bourrat et al. [1]. Applying the new terminology for carbon textures [2], OA values from 20 to 50° were considered to correspond to highly textured (HT) pyrocarbon. Medium textured (MT) pyrocarbon is characterized by OAs between 50 to 80°.

AFM measurements were performed with an Autoprobe CP atomic force microscope (Park Scientific Instruments). Commercially available Si<sub>3</sub>N<sub>4</sub>-coated cantilevers with force constants between 0.02 and 0.1 N/m were used. The total normal force (including capillary forces) was several 10<sup>-8</sup> N.

### Results

The layer thickness and a coarse impression of the texture were obtained by SEM surface analysis of fractured cross-section samples. For the layers deposited without O<sub>2</sub>, the thickness increases as a function of the

substrate length (residence time). A transition from MT to HT carbon is observed with increasing  $\tau$ . This result is confirmed by the orientation angles which decrease from 78° at  $\tau = 1.2$  s to 37° at  $\tau = 2$  s.

For residence times below 1 s, the deposited carbon does not form a continuous layer. SEM and AFM images of the substrates surface reveal that isolated islands occur during the earliest stage of the carbon deposition with typical islands sizes from 30 to 60 nm. The density of the islands increases with the residence time until a closed carbon layer is obtained.

For the layers deposited with 3 % O<sub>2</sub>, the thickness increase follows the same trend as without O<sub>2</sub>. However, the growth rate is reduced compared to the pure argon / methane gas mixture. The texture of the layer displays a completely different behaviour than without oxygen. HT carbon is obtained for lower residence times at small deposition rates, whereas MT carbon occurs at higher values of  $\tau$ .

AFM investigations were performed at  $\tau = 1.8$  s for 0, 0.1, 1 and 3 % O<sub>2</sub>. The surfaces of the closed layers are generally characterized by island-like structures similar to the isolated islands at small residence times. The O<sub>2</sub> concentration affects the size of the island-like structures which increases up to 120 nm at 3 % O<sub>2</sub> while their density is not strongly affected.

### Discussion and Conclusion

The experimental results for the depositions *without oxygen* show that the residence time increase leads to an increase of the deposition rates and a transition from MT to HT pyrocarbon. As a general trend, low deposition rates are always correlated with low and medium texture degrees while highly textured pyrocarbon is formed at high deposition rates. The transition from MT to HT carbon with increasing  $\tau$  can be exploited to qualitatively correlate the size of the molecular species in the gas phase with the texture of the deposited material. It is reasonable to assume that small hydrocarbon molecules are correlated with small residence time while larger (poly)aromatic species are formed at higher  $\tau$  by gas phase reaction. Therefore it can be concluded that - at least in the chosen range of residence times - the deposition from small hydrocarbon species leads to medium texture degrees. The deposition of HT carbon requires obviously the preformation of larger hydrocarbon molecules as suggested in Ref. [3].

SEM and AFM analyses allow the characterization of the earliest stages of the carbon deposition. The results show that isolated islands are first deposited. The increase of the residence time leads to higher island



densities and finally to the formation of a continuous carbon layer.

A significant influence of oxygen on the deposited pyrocarbon could be detected. The deposition rate is generally lower than without oxygen. The additional supply of oxygen can be exploited to influence the pyrocarbon texture because HT pyrocarbon was obtained at low residence times and deposition rates. Finally, different islands sizes occur with and without oxygen. These observations indicate that small oxygen concentrations affect the type of molecules and composition of the gas phase.

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