QUANTITATIVE ANALYSIS OF PYROLYTIC CARBON FILMS BY POLARIZED LIGHT MICROSCOPY

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Abstract

The optical properties of differently textured pyrolytic carbon films were quantitatively analyzed by polarized light microscopy. The light intensity for the investigation of optically anisotropic and birefringent materials by polarized light microscopy was calculated as a function of the analyzer angle and the orientation of the material. From these calculations the dependence of the extinction angle on the optical properties of the material such as the reflection coefficients for ordinary and extraordinary rays and their relative phase shift was determined for flat as well as for cylindrical carbon layers [1]. These calculations are not only essential for an understanding of the characterization of pyrolytic carbon films by polarized light microscopy but also for an understanding of the correlation between extinction angles measured for flat and for cylindrical pyrolytic carbon layers.

Pyrolytic carbon films deposited on flat cordierite substrates were studied by polarized light microscopy. From the fit of the experimental data, reflection coefficients and their relative phase shifts could be quantitatively determined for differently textured pyrolytic carbon layers. Extinction angles as high as 21° were measured on flat substrates.

Introduction

Polarized light microscopy has been used for decades as a method that is well suited for a fast characterization of the degree of texture of pyrolytic carbon. For the fast optical characterization of flat pyrolytic carbon films, cross-sections perpendicular to the substrate surface are investigated. Polarized light is used for illumination and the analyzer is rotated until a minimum in intensity is reached. The angle of the analyzer at this minimum is called the extinction angle.

The correlation between the extinction angle and the optical properties of pyrolytic carbon films, however, has not been understood in detail. Only recently, the difference between extinction angles determined on pyrolytic carbon films deposited on flat substrates and on deposits with a circular symmetry (e.g. pyrolytic carbon films grown on carbon fibers) was pointed out [1, 2].

Here, we report on (i) experimental investigations of pyrolytic carbon films by polarized light microscopy, (ii) the corresponding theoretical description of this experiment and (iii)

the application this theoretical description on the experimental data, leading to a consistent quantitative understanding of the polarized reflectance data. The reflectivities for the ordinary and extraordinary rays and the phase shift between the reflection coefficients for ordinary and extraordinary rays are deduced from a fit of the experimental data using a calculated intensity profile.

Experimental

Pyrolytic carbon films were deposited in a hot wall reactor at a temperature of 1100 °C from pure methane. Channel structures consisting of cordierite ($Mg_2Al_4Si_5O_{18}$) with a ratio of surface area to free volume of 0.79 mm^{-1} were used as substrates. Pyrolytic carbon films deposited at methane partial pressures of 4 kPa (deposition time 30 h) and 37.5 kPa (deposition time 185 h) were investigated. The gas flow within the reactor was in the vertical direction from the bottom to the top of the reactor to avoid convection. The gas flow was adjusted to reach a maximum residence time τ of 1 s at the end of the cordierite substrate. The deposition time was chosen long enough to deposit films that are thick enough to allow an investigation by light microscopy. For each of the two methane pressures, flat samples were cut from the top of the channel structure (residence time 0.875 s). For the case of 4 kPa methane pressure, a second flat sample was cut from the bottom of the channel structure (residence time 0.125 s). Details of the deposition process are described elsewhere [3, 4]. The texture of the pyrolytic carbon films investigated by polarized light microscopy in this work was characterized by selected area electron diffraction by Hu et al. ([4], see Table 1) using an aperture with a diameter of 2.5 µm.

Light microscopy was carried out using a DM LM Microscope (Leica, Wetzlar, Germany) equipped with polarizer and analyzer. Neutral grey filters (Itos, Mainz, Germany) with a known transmission coefficient and a gold mirror with known reflectivity were used to normalize the light intensity after the analyzer to the light intensity after the polarizer.

Results and Discussion

Graphite which is considered the high-order limit for pyrolytic carbon is optically anisotropic and birefringent: graphite is negative uniaxial. The reflectivity for ordinary rays R_o (vector of the electrical field perpendicular to the optical axis) is larger than the reflectivity for extraordinary rays R_e (vector of the electrical field parallel to the optical axis).

In the following, the light intensity measured after the analyzer for the investigation of optically anisotropic and birefringent materials by polarized light microscopy will be calculated in dependence on the intensity of the illuminating polarized light, the orientation of the optical axis of the sample relative to the polarization of the incoming light, the optical properties of the sample such as the reflection coefficients for ordinary and extraordinary rays and their relative phase shift and the angle of the analyzer. These calculated intensities will be compared with experimental data to show that pyrolytic carbon films with different degrees of texture can indeed be described as optically anisotropic and birefringent.

Figure 1 shows the geometry of the experiment and the quantities used for the calculation of the light intensity after the analyzer. α denotes the angle between preferred orientation of the layers and the direction of the polarizer (i.e. the polarization direction for maximum transmission). First, the vector of the electric field of the incoming polarized light $\mathbf{E_e}$ is projected onto the direction of the preferred orientation of the graphene layers and onto the direction perpendicular to this orientation. The reflection at the sample surface is described by a multiplication of the electrical field vectors with the respective complex reflection coefficients $\mathbf{r_o}$ (vector of the electrical field perpendicular to the optical axis) and $\mathbf{r_e}$ (vector parallel to the optical axis). The electrical field vector after reflection $\mathbf{E_r}$ is the vector sum of the two components.

The electrical field $\boldsymbol{E}$ after the analyzer can be calculated by the projection of $\mathbf{E_r}$ onto the direction of the analyzer:

$$E \propto \sqrt{r_e \sin^2 \alpha + r_o \cos^2 \alpha} \, \cos(\phi + \arctan(\frac{r_e}{r_o}\tan\alpha) - \alpha) \tag{1}$$

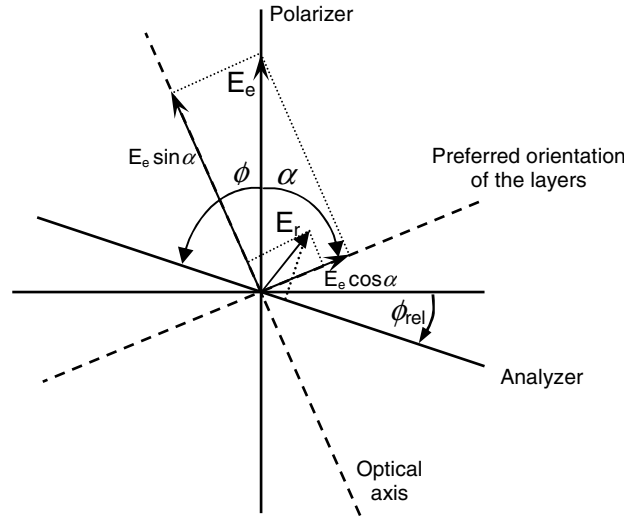where ϕ is the angle between analyzer and polarizer.

Figure 1: Geometry used for the determination of extinction angles and the notations used for the calculation of the light intensity.

The square of (1) gives the intensity I after the analyzer:

$$I = \left|\vec{E}\right|^2 \propto r_e^2 \sin^2\alpha \cdot \sin^2(\alpha - \phi) + r_o^2 \cos^2\alpha \cdot \cos^2(\alpha - \phi)$$

$$+ \frac{1}{2}r_e r_o \cos\Delta \sin 2\alpha \cdot \sin(2(\alpha - \phi)) \tag{2}$$

where Δ is the phase shift between the complex reflection coefficients $\textbf{\textit{r}}_o$ and $\textbf{\textit{r}}_e$. r_o and r_e are the absolute values of $\textbf{\textit{r}}_o$ and $\textbf{\textit{r}}_e$.

For the investigation by polarized light microscopy, flat samples are usually oriented with the preferred orientation of the layers at an angle of 45° relative to the direction of the polarizer. This results in the intensity $I_{45°}$:

$$I_{45°} \propto \frac{1}{2}\left[r_e^2 \cdot \sin^2(45° - \phi) + r_o^2 \cdot \cos^2(45° - \phi) + r_e r_o \cos\Delta \cdot \cos 2\phi \right] \qquad (3)$$

The angle of the analyzer for minimum intensity relative to the direction perpendicular to the polarizer (compare ϕ_{rel} in Figure 1) is given by (see [1]):

$$\phi_{rel,45°} = \frac{1}{2}\left(\arctan \frac{2\dfrac{r_e}{r_o}\cos\Delta}{\dfrac{r_e^2}{r_o^2} - 1} \right) - 45° \qquad (4)$$
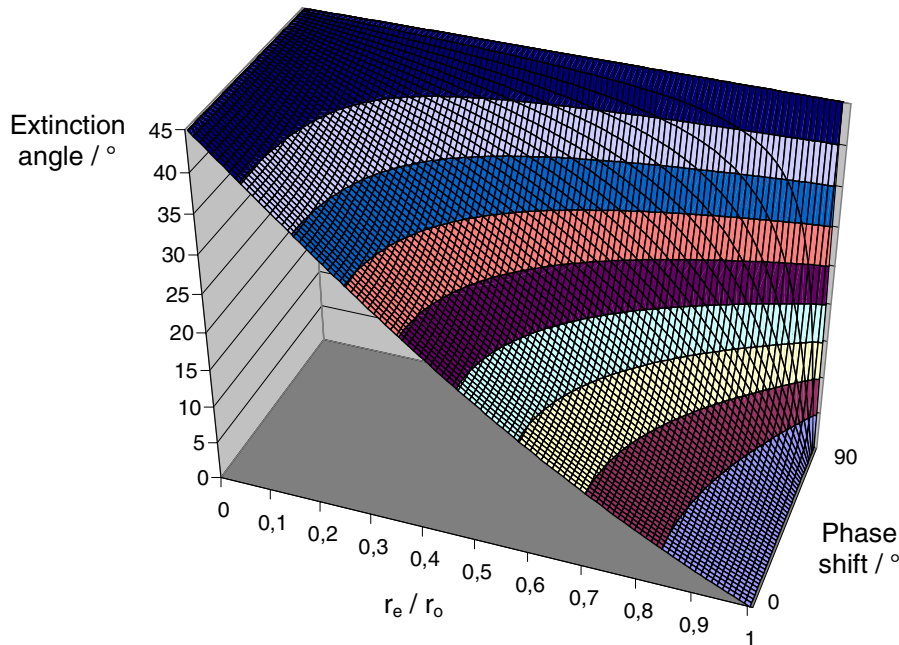

Figure 2: The dependence of the extinction angle on the ratio r_e / r_o and the phase shift Δ calculated for the case of flat samples.

Figure 2 shows the dependence of the extinction angle on the ratio r_e / r_o and the phase shift Δ calculated for the case of flat samples. The extinction angle increases

monotonously with increasing degree of anisotropy of the reflection coefficients. Furthermore it increases monotonously with increasing phase shift, even though the dependence on the phase shift is not as strong as for samples with rotational symmetry (see [1]).

Having calculated the intensity dependence on the analyzer angle and the correlation with optical parameters of the investigated films like r_e, r_o and Δ, the results of polarized optical microscopy on pyrolytic carbon films can now be analyzed quantitatively.

Figures 3a-c show cross-sectional images of the investigated samples taken by polarized light microscopy at an angle of the analyzer of 0°. The cordierite substrate appears dark whereas the pyrolytic carbon shows up brighter. The substrate contained open pores which were infiltrated with pyrolytic carbon (see arrow in Figure 3a). The cross-sections of Figure 3 show that the pyrolytic carbon film itself, which was grown on top of the cordierite substrate is not homogeneous, but consists of growth cones. Within the growth cones the local preferred orientation of the carbon layers on the µm-scale is not constant but can deviate from the macroscopic orientation of the film parallel to the substrate. For this reason it is not only important to chose an area for the evaluation of the intensity that is free of contaminations but the preferred orientation of the carbon layers must also correspond to the macroscopic orientation of the pyrolytic carbon film. Once an appropriate area is selected, the average intensity in this area is determined.

The normalized light intensities determined experimentally are plotted versus the angle of the analyzer in Figures 3d–f as squares for the three investigated samples. As expected from the calculation, in all cases one minimum and one maximum were found.

Previously the characterization of pyrolytic carbon films was done by finding the extinction angle (i.e. the angle of the analyzer at minimum intensity given as Ae_{Min} in Table 1). In this work, the additional effort of determining the normalized intensity gives access to additional information on the optical properties of pyrolytic carbon films. For this purpose the measured data were fitted with the calculated intensity given in (3) (see solid curves in Figure 3d – f). The formula for the intensity is symmetric in Δ, which allows only the determination of the absolute value of Δ. The parameters Ae_{fit}, Δ and R_o that were adjusted in the fitting process are given in Table 1 together with the values r_e/r_o and R_e that were calculated from the former three values:

Sample	Ae_{Min}	Ae_{fit}	$|\Delta|$	R_o	R_e	r_e/r_o	OA [4]
$p_{methane}$ = 4 kPa, τ = 0.125 s	11°	10.3°	20.9°	0.15	0.077	0.71	63°
$p_{methane}$ = 4 kPa, τ = 0.875 s	12°	11.8°	21.6°	0.16	0.070	0.67	57°
$p_{methane}$ = 37.5 kPa, τ = 0.875 s	21°	21.6°	29.0°	0.22	0.050	0.47	26°

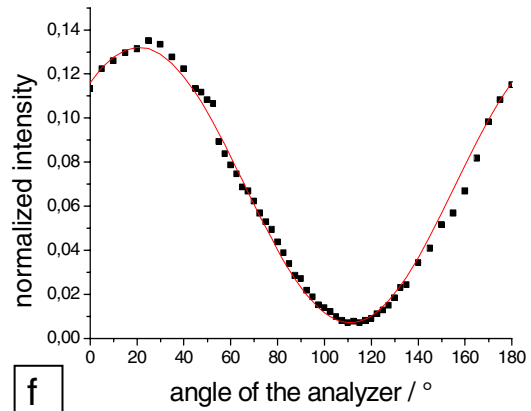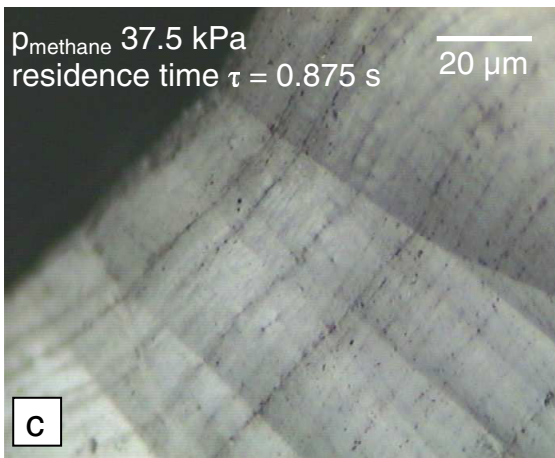Table 1: Optical parameters derived from the experimental data and from the fits of these data shown in Figures 3d–f.
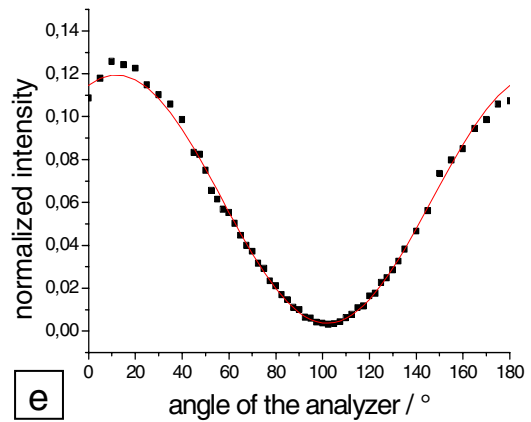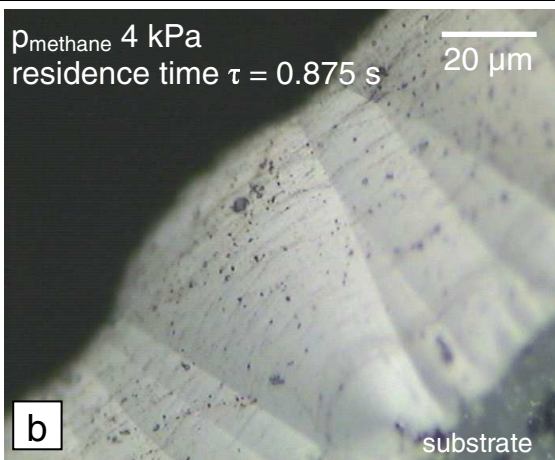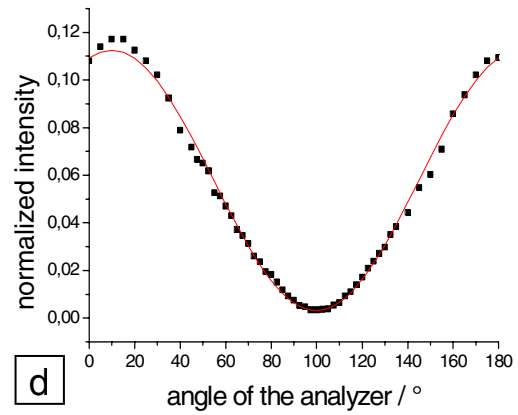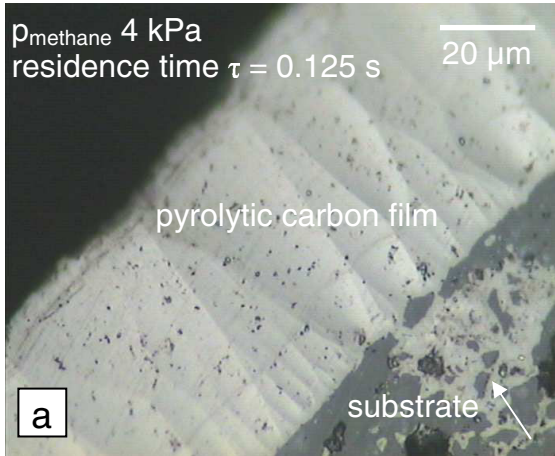
Figure 3: Polished cross-sections of pyrolytic carbon films with different degrees of texture on cordierite investigated by polarized light microscopy. a) – c) Images taken by polarized light microscopy, 126 µm x 95 µm, analyzer parallel to polarizer, d) – f) normalized light intensity vs. angle of the analyzer. The squares correspond to the experimental data. The solid line is calculated according to (3) by fitting the parameters A_e, Δ and R_o.

A good agreement between experimental data and calculated curves was found for all three samples, i.e. for pyrolytic carbon with different textures. The extinction angles determined directly (Ae_{Min}) and determined from the fit curve (Ae_{fit}) correspond within the expected error of about 1° for the direct determination. All other optical parameters ($|\Delta|$, R_o, R_e, r_e/r_o) show a monotonous behavior with extinction angle or degree of texture.

Conclusions

The texture was investigated at µm scale by both, selected area electron diffraction and polarized light microscopy. For selected area electron diffraction an aperture with a diameter of 2.5 µm was used. Following the definition by Reznik et al. [5] the two films deposited at a methane pressure of 4 kPa (see Figure 3a, b) can be classified as medium-textured by considering the orientation angle. The other film deposited at a methane pressure of 37.5 kPa is high-textured (see Figure 3c). One should emphasize that the sequences of the degrees of texture determined by polarized light microscopy and selected area electron diffraction are consistent although the two different techniques were not performed at the same location on the sample.

It is expected that the anisotropy of the optical properties decreases with the decrease of the degree of texture. This is confirmed by the data derived from the experiment, as r_e/r_o, the anisotropy factor of the reflection coefficients, decreases. Also the reflectivities follow this expectation: R_o increases whereas R_e decreases with an increase of the degree of texture.

The monotonous dependence of all optical parameters on the texture might indicate that one variable, e.g. the extinction angle is sufficient for the description of the texture at one length scale, in this case at the µm-scale. Further systematic investigations are necessary to clarify this point.

The maximum extinction angle determined in this study was 21°, a value that lies well above the extinction angles for graphite expected from most data sets for the optical properties of graphite in literature (this value can be calculated from (4)). For example Bortchagovsky et al. [1] calculated an extinction angle of 17.9° for graphite using data from Ergun et al. [6]. The measurement of an extinction angle of 21° for pyrolytic carbon also shows that either the optical anisotropy of graphite as the high-order limit for pyrolytic carbon or the phase shift Δ between the reflection coefficients r_o and r_e of graphite is significantly higher than previously expected.

To conclude, in this paper a new method for the quantitative analysis of the optical properties of pyrolytic carbon films was presented. Flat pyrolytic carbon films with different degrees of texture were experimentally characterized by polarized light microscopy. By analyzing the data, in addition to the extinction angle, the absolute values of the reflection coefficients r_e and r_o and their relative phase shift Δ were quantitatively determined.

Acknowledgements

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