

Supporting information for: Orientation of Non-Planar Molecules in Polycrystalline Layers from Infrared Spectra: Core-Chlorinated Naphthalene Tetracarboxylic Diimides

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Comparison to transmittance measurements

To support the discussion of the orientation of the molecules obtained from ellipsometric measurements and DFT calculations, relative IR transmittance measurements were carried out on a sample of 55 nm NDI-F evaporated on both-sides polished Si at incident angles of $\Phi_1 = 0^\circ, 30^\circ, 60^\circ, 75^\circ$ with p-polarized light and a resolution of 4 cm^{-1} . The reference was a bare Si wafer. The uniaxial anisotropy of polycrystalline films effects that as the incident angle of the EM-wave measured against the substrate normal increases, the absorption caused by infrared-active modes oscillating predominantly perpendicular to the sample is increased. If the dipole vector of the oscillation is oriented predominantly parallel to the sample the absorption is decreased. This effect as well as a comparison of transmittance spectra, ellipsometry spectra and DFT calculation is shown in ???. For a comparison between ellipsometric and transmittance measurements we plotted calculated transmittance spectra obtained from the dielectric function that was derived from modeling ellipsometry spectra. A good correspondence between the two methods is found above 550 cm^{-1} . Below the signal to noise ratio in the transmittance spectra is insufficient for a comparison. Deviations will be discussed in the following.

The mode at 603 cm^{-1} is modeled as an oscillation perpendicular to the sample surface whereas it clearly shows the behavior of a parallel mode in the transmittance measurements. We suppose that the two phonon peak of the silicon substrate located at 613 cm^{-1} (TO+TA)[?] could lead to wrong modeling of the ellipsometry spectra as the signal of the multiphonon peak is considerably stronger than the signal from the molecular oscillation.

The deviations in the range from $850 - 950\text{ cm}^{-1}$, at 1183 cm^{-1} and 1368 cm^{-1} might be due to a significant dipole component parallel to the surface, whereas they were modeled as perpendicular only. Note that each oscillation was modeled as either completely perpendicular or parallel to the substrate surface.

The discrepancy in the transmittance spectra at 1108 cm^{-1} can be attributed to slightly different amounts of oxygen in the sample substrate and the wafer used for the reference spectrum.[?]

In the ellipsometry measurements the signal of the mode at 1568 cm^{-1} is only slightly above the

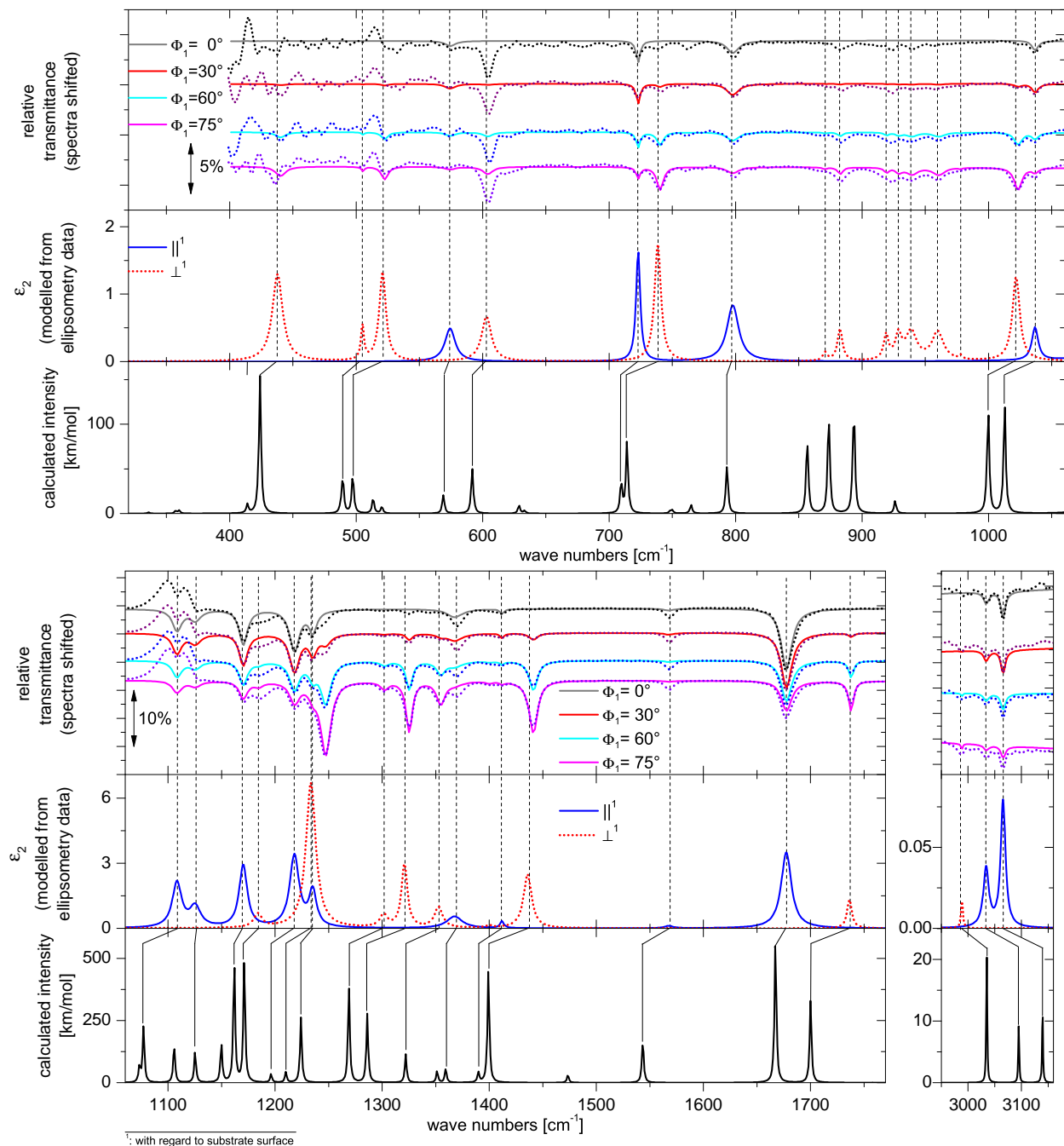


Figure 1: Top: Measured (dotted line) and calculated (solid line) relative IR transmittance spectra of a NDI-F layer evaporated on silicon. Middle: imaginary part of the dielectric function for a NDI-F layer on silicon derived from ellipsometry measurements. Bottom: DFT calculation for the intensity of dipole oscillations. The transmittance spectra were measured at different incident angles. The calculated transmittance spectra were obtained by means of the dielectric function that in turn was derived from modeling ellipsometry spectra. Note that the transmittance spectra were shifted against each other along the ordinate for clarity. The broken lines indicate the position of peaks modeled in ellipsometry spectra. The DFT peaks were broadened with $\gamma = 1 \text{ cm}^{-1}$ for optical agreement. The area under a peak corresponds to the calculated intensity.

signal to noise ratio whereas the mode is clearly visible in the transmittance spectra. It is possible that both Fresnel coefficients change by the same amount along the spectra with the result that their ratio stays constant. Thus it is hardly detectable in our ellipsometry measurements. Hence the behavior in the transmittance spectra is not calculated correctly.

Table 1: Best-fit parameters for all measured oscillators according to eq. 3, DFT results for resonance frequencies, and designation of corresponding molecular vibration. The vibrations used for the orientation analysis (see section about molecular orientation) are marked with asterisks. The experimentally derived orientation with regard to the substrate plane is also given. ω_i , S_i , γ_i , and $\omega_{i,\text{DFT}}$ are given in units of $[\text{cm}^{-1}]$, the DFT calculated oscillator strength $S_{i,\text{DFT}}$ in $[\text{km/mol}]$

ω_i	S_i	γ_i	$\omega_{i,\text{DFT}}$	$S_{i,\text{DFT}}$	Mode
out-of-plane					
439	9(2)	7(2)	424.0	154.5	$\delta\text{-CO}$, $\delta\text{-CH}$, $\delta\text{-CH}_2$, NDI plane
505	1	3	489.5	40.1	$\delta\text{-CH}$, $\delta\text{-CH}_2$, $\delta\text{-CO}$, NDI plane
521	6.1(9)	5(1)	497.4	43.7	$\nu\text{-CH}$, $\delta\text{-CF}_3$, $\delta\text{-CH}_2$, NDI plane
603	6.2(7)	9(1)	591.8	51.3	$\delta\text{-CH}$, $\delta\text{-CH}_2$, NDI plane
739	9.2(4)	5.4(4)	714.2	81.5	$\delta\text{-CF}_3$, $\delta\text{-CH}$
871	0.7(3)	5(3)			
882	2.5(3)	5.1(9)			
919	1.8(3)	5(1)			
929	2.3(3)	6(1)			
939	4.7(4)	11(1)			
960	4.9(3)	12(1)			
978	0.1	2			
1022	9.5(3)	7.5(3)	999.7	118.2	$\delta\text{-CH}$
1184	5.1(4)	8(1)	1173.3	486.3	$\delta\text{-CF}$, $\delta\text{-CH}_2^$
1234	72.5(4)	10.7(1)	1210.0	41.4	CF_2 wagging, $\delta\text{-CF}_3$
1301	5.3(2)	9.3(6)	1268.9	379.8	$\delta\text{-CF}_2$, $\delta\text{-CF}_3^$

Table 1: (continued)

	ω_i	S_i	γ_i	$\omega_{i,\text{DFT}}$	$S_{i,\text{DFT}}$	Mode
1321	19.4(2)	6.6(1)	1286.0	276.6		δ -CNC, δ -CH
1353	9.1(1)	9.4(2)	1322.0	114.6		CH ₂ twisting
1400	0.5(2)	6(3)				
1436	22.2(2)	8.9(1)	1399.2	463.5		NDI plane
1736	7.6(2)	5.7(2)	1700.1	329.6		ν -CO
2987	0.1	6	3035.0	δ -CH ₂		
in-plane						
574	5	10	568.93	20.6		δ -CH, δ -CO, δ -CH ₂ , NDI plane
723	9.3(9)	5.8(8)	709.6	34.0		δ -CO, CH ₂ twisting, NDI plane
797	14(1)	17(3)	793.2	53.8		NDI plane, ν -CF ₂ , δ -CH
1037	3.6(8)	8(2)	1012.8	125.5		δ -CH
1108	17.9(6)	8.4(4)	1077.1	222.7		CF ₂ wagging, δ -CF ₂
1125	9.0(6)	10(1)	1125.3	127.4		δ -CF ₂ , δ -CF ₃
1170	24.9(6)	8.6(3)	1161.8	478.6		δ -CF ₂ , CF ₂ wagging
1218	37.1(8)	11.2(3)	1196.2	34.0	δ -CH	
1235	15.1(7)	9.2(6)	1224.1	265.1		δ -CH
1368	9	17	1359.3	57.1		δ -CH, naphthalene
1412	3.2(6)	11(3)	1389.8	40.9		δ -CH ₂
1566	1.2	11	1543.4	171.6		naphthalene, δ -CH
1677	39.0(6)	11.1(2)	1667.3	588.7		ν -CO
3034	0.4	11	3095.0	9.1		
3066	0.8	9	3139.6	12.2		