Sub-nanoscale surface displacement detection in thin films using mid-IR photothermal- mirror spectroscopy & - scanning probe microscopy

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Introduction

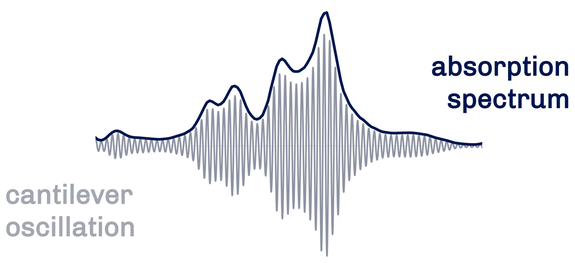
01

In this work, we apply two notable techniques for the characterization of thin polymer films: Photothermal Mirror Spectroscopy (PTM) and Scanning Probe Microscopy- Infrared Spectroscopy (AFM-IR). PTM allows insights into thermal diffusivity and optical absorption coefficient of the sample and this technique was adapted for the first time for thin polystyrene (PS) films. On the other hand, AFM-IR combines high-spatial resolution beyond the diffraction limit combined with the chemical specificity of mid-IR spectroscopy. The results then were compared to state-of-the-art FT-IR and showed good agreement. By plotting the marker band signal of PS against the film thicknesses a good linearity could be shown.

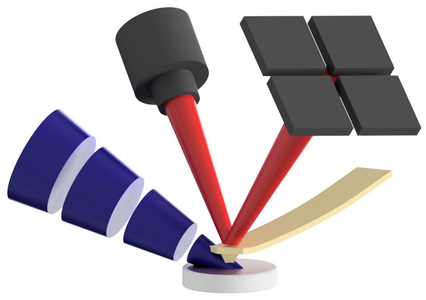
AFM-IR, a photothermal technique

02

Mid-Infrared spectroscopy is a powerful technique for identification of functional groups and chemical bonds, but it is limited due to the long wavelength of mid-IR, thus constraining the spatial resolution. **AFM-IR** overcomes this by combining scanning probe microscopy with mid-IR and thus combines high-spatial resolution with chemical specificity of mid-IR spectroscopy.



A local, **short-lived thermal absorption** of IR-light induced by a pulsed, tunable EC-QCL source, is measured by the sharp tip of a cantilever. Here, the oscillation amplitude is proportional to the optical absorption coefficient [1].



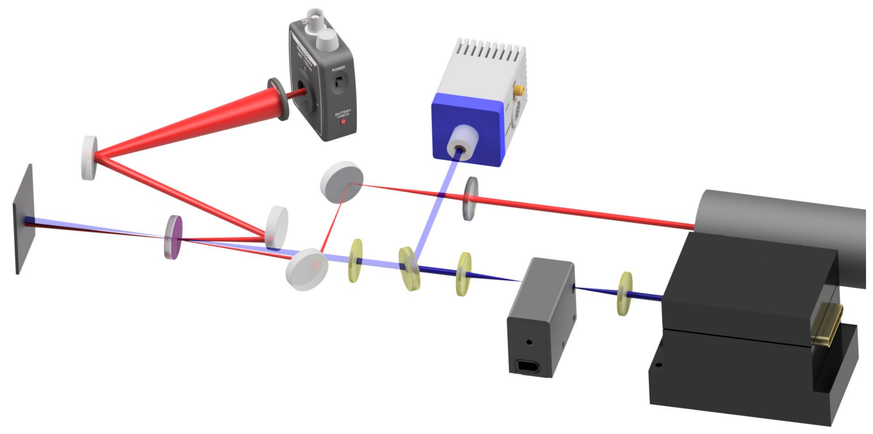
Schematic for the AFM-IR measurements. Red laser is the deflection laser, read out by a four-quadrant photodiode. Blue laser is a pulsed, tunable, EC-QCL (5.04 µm – 11.11 µm).

Thus, by tuning the wavelength of the infrared laser, absorption spectra - or by keeping the wavelength fixed and scanning the AFM tip, absorption images can be recorded.

PTM, the photothermal mirror

03

PTM or photothermal mirror spectroscopy is like AFM-IR an indirect, non-destructive technique taking advantage of photothermal excitation of the sample for performing mid-IR spectroscopy.
Here, a **modulated mid-IR beam** is used for the excitation of the sample. This periodic deformation of the sample area, induced by the excitation laser, can be detected, non-destructively with a collinear **He-Ne laser** and the intensity variation of the probe beam center after reflection on the sample surface is detected by a **pin-hole photodetector.** A lock-in amplifier demodulates then the PTM signal and the excitation signal.



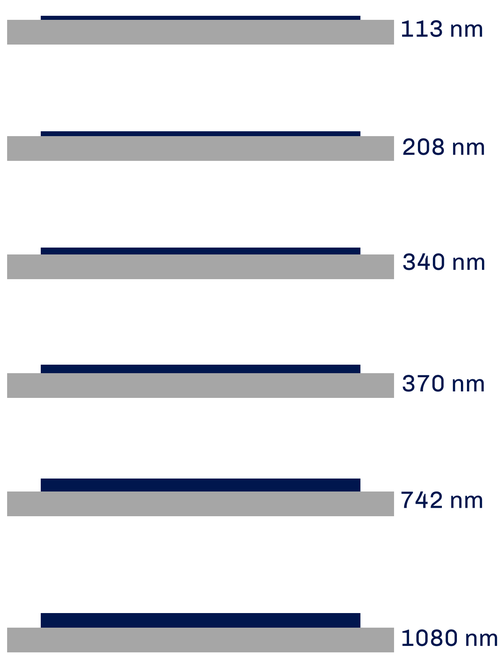
Schematic for the experimental PTM measurements. Red laser is a He-Ne laser (632.8 nm). Blue laser is a tunable, continuous wave EC-QCL (5.79 µm – 6.75 µm). Detection of excitation beam by an MCT detector and of the probe laser by a photodiode, respectively.

The PTM technique allows insights into thermal diffusivity and optical absorption coefficient of the sample and thus can be applied for characterization of materials, such as glasses [2] metals [3], etc.

Thin-film polymers

04

Polystyrene (PS) thin films were investigated in this work and were created by spin coating on wedged CaF_2 windows.



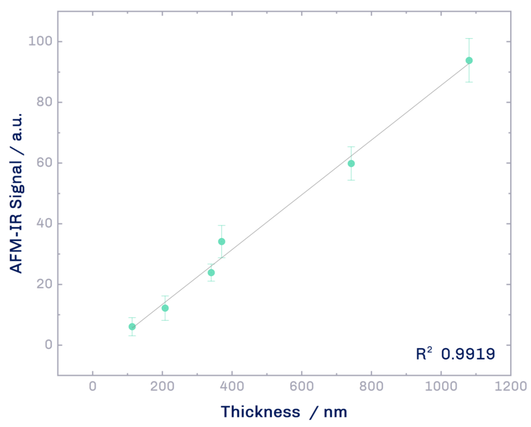
Thin films were prepared using same spin coating parameters with concentrations ranging from 1,7 wt% - 8 wt%.

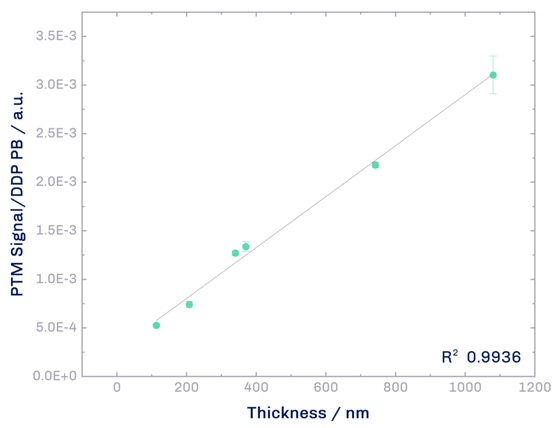
The PS film thicknesses were then determined using a profilometer. Additionally surface roughness measurements were conducted, and the arithmetic mean roughness (R_a) and the arithmetic mean waviness (W_a) recorded.

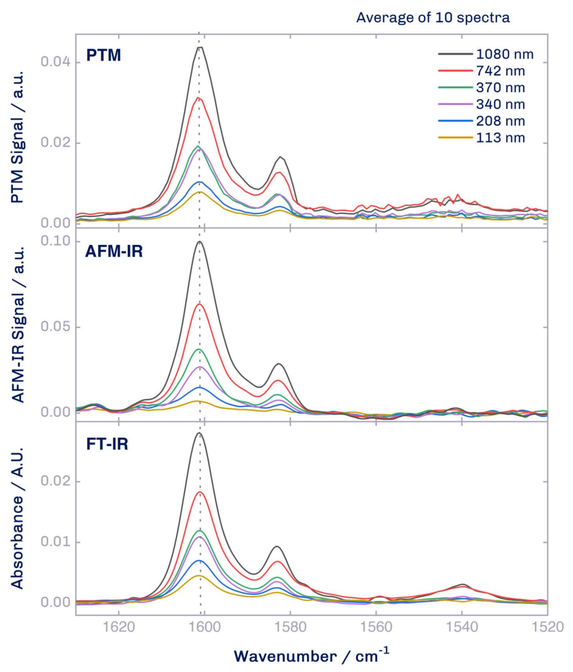
Results

05

PS thin film spectra are recorded with PTM and AFM-IR and compared to FT-IR measurements. As we investigate PS, we focus on the aromatic ring stretching vibration at 1601 cm^{-1}. The additional aromatic ring modes at 1492 cm^{-1} and 1451 cm^{-1} are not plotted due to the limited spectral coverage of the EC-QCL (for PTM). All three techniques exhibit characteristic bands at 1601 cm^{-1} and 1583 cm^{-1}, which can be assigned to the aromatic ring stretching of PS.
A further band appears at 1540 cm^{-1} but only clearly visible in FT-IR. The band positions as well as the band shapes are throughout the three techniques comparable. The signal intensity of the marker band of PS at 1601 cm^{-1} is plotted below against the polymer film thicknesses and shows a good linearity.







Conclusions

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- ✓ We adapted the photothermal mirror technique for mid-IR spectroscopy measurements.
- ✓ We measured a range of polymer thin film thicknesses with PTM, AFM-IR & FT-IR.
- ✓ The feasibility of the technique for thin film materials is shown.

[1] A. Dazzi, F. Glotin, and R. Carminati, Theory of infrared nanospectroscopy by photothermal induced resonance, Applied Physics 107, 124519 (2010) DOI: 10.1063/1.3429214
[2] Lukasievicz, G. V. B.; Astrath, N. G. C.; Malacarne, L. C.; Herculano, L. S.; Zanuto, V. S.; Baesso, M. L.; Bialkowski, S. E. Pulsed-Laser Time-Resolved Thermal Mirror Technique in Low-Absorbance Homogeneous Linear Elastic Materials, Appl Spectrosc 2013, 67 (10), 1111–1116 DOI: 10.1366/13-07068
[3] Lukasievicz, G. V. B.; Malacarne, L. C.; Astrath, N. G. C.; Zanuto, V. S.; Herculano, L. S.; Bialkowski, S. E. A Theoretical and Experimental Study of Time-Resolved Thermal Mirror with Non-Absorbing Heat-Coupling Fluids. Appl Spectrosc 2012, 66 (12), 1461–1467. DOI: 10.1366/12-06743.

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