
Ellipsometry and Atomic Force Microscopy on Polymer Films

Advanced physical lab exercises

Lab course, Working Group "Soft Matter at Interface"

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1 Introduction

In this experiment, the silicon wafers are coated with polystyrene by spin coating, and the effect of various parameters is investigated. For this purpose, the layer thicknesses are measured with Ellipsometry and the surfaces' structure are analysed by atomic force microscopy. The focus is on the theoretical principles of polymer coatings, further on the principles and the functionality of the individual measurement methods. The experimental results are compared with the theoretical models.

$$h_f = (1 - c_0)h_w = (1 - c_0) \left[\frac{3\mu_0}{2\rho\omega^2} k(c_0 - c_\infty) \right]^{\frac{1}{3}} \quad (1)$$

where $k \propto \omega^{\frac{1}{2}}$

$$\propto \mu_0^{\frac{1}{3}} \omega^{-\frac{1}{2}} (1 - c_0)(c_0 - c_\infty)^{\frac{1}{3}} = \mu_0^{\frac{1}{3}} \omega^{-\frac{1}{2}} \left[(c_0 - c_\infty)^{\frac{1}{3}} - c_0(c_0 - c_\infty)^{\frac{1}{3}} \right] \quad (2)$$

Where h is the layer thickness, ω the rotation speed and μ the viscosity of the solution.

2 Theoretical principles

Note: The chapter is only presenting a short overview. The detailed preparation has to be developed independently on the basis of the given original literature.

2.1 Polymer Coating

The miniaturization of the electronic component, weight reduction with improved mechanical stability, and the desire for space-saving justify the technical interest in producing thin and ultrathin polymer coatings and films. Coating thicknesses under 200 nm are known as an ultrathin coatings[1]. The polymer coatings are interesting for both optical sensors and also for microelectronics[1].

2.2 Spin Coating

Over the years, many techniques have been developed to produce polymer films. Here for the possibility of work on an industrial scale both reproducibility and also technical applications are important. Spin coating has been established as a strong method to produce films in a wide range of thickness, typically from 10 nm to 2000 nm. Other established techniques are dip coating and spray coating (pages 1 - 12 [2]).

For spin coating, a polymer solution is applied on a solid substrate. The solution will move uniformly on the substrate through rotation and Centrifugal force. Homogeneous coating is formed depending on the concentration of the polymer solution, the solvent, and the speed of the rotation [1].

2.3 Ellipsometry

Ellipsometry is a fast, non-destructive method to characterize thin films. Thereby, layer thickness and refractive index are determined (pages 2 - 10 [3] and pages 21 - 24 [4]). A polarized Laser beam generated with a polarizer and compensator is reflected from a thin layer and the change in polarization is analyzed with the analyzer (ellipsometer in PCSA configuration). The electric field vector can be divided into a component E_p , oscillating parallel to the plane of incidence and component E_s , oscillating perpendicular to the plane of incidence. The incident and reflected beams, \vec{E}_{inc} and \vec{E}_{refl} , can be described by the corresponding Jones vectors:

$$\vec{E}_{inc} = \begin{pmatrix} |E_p^i| e^{i\delta_p^i} \\ |E_s^i| e^{i\delta_s^i} \end{pmatrix} \quad (3)$$

$$\vec{E}_{refl} = \begin{pmatrix} |E_p^r| e^{i\delta_p^r} \\ |E_s^r| e^{i\delta_s^r} \end{pmatrix} \quad (4)$$

The change of the polarized light can be described by the ellipsometric angles Ψ and Δ .

$$\tan \Psi = \frac{|E_p^r|/|E_p^i|}{|E_s^r|/|E_s^i|} \quad (5)$$

$$\Delta = (\delta_p^r - \delta_s^r) - (\delta_p^i - \delta_s^i) \quad (6)$$

According to equation 7, using ellipsometric angles Ψ and Δ can calculate ratio of the parallel reflectivities R_p (reflectivity for p-polarized light) over perpendicular reflectivities R_s (reflectivity for s-polarized light) to the plane of incidence.

$$\frac{R_p}{R_s} = \tan \Psi e^{i\Delta} \quad (7)$$

Here Δ and Ψ are not geometrical angles, nevertheless, are related to the angular position of polarizer before and after reflection. $\tan(\Psi)$ defines the magnitude of the reflectivity ratio for p-polarized and s-polarized light, and Δ defines the phase difference between the reflected p-polarized and s-polarized light.

In Null-Ellipsometry (see Fig.1) experiment uses the quarter $\lambda/4$ -wave plates as compensation and the following relationship: (Unfortunately it was my best :

$$\tan \Psi e^{i\Delta} = \frac{R_p}{R_s} = \tan A_0 \cdot \exp^{i(2P_0 + \frac{\pi}{2})} \text{ for } C = -45^\circ \quad (8)$$

$$\tan \Psi e^{i\Delta} = \frac{R_p}{R_s} = -\tan A_0 \cdot \exp^{i(\frac{\pi}{2} - 2P_0)} \text{ for } C = 45^\circ \quad (9)$$

Where C is the angular value of the compensator and when the light is completely extinguished P_0 and A_0 are the angular values of the polarizer and analyzer respectively.

<http://www.overleaf.com>

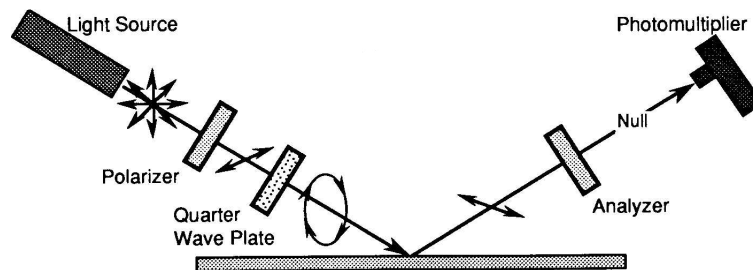


Fig. 1: Scheme of zero ellipsometry: Light from a light source is polarized in a linear polarizer. A subsequent $\lambda/4$ -plate generates elliptically polarized light which is reflected at the sample. The linearly polarized light after reflection is cancelled in an analyzer. Taken from: http://www.fis.unipr.it/~gigi/elli/principi_ellissometria.html

The following video explains the basic principles of Ellipsometry: <https://www.youtube.com/watch?v=BycPkRIutqg>. The first part of the video introduces the principle of ellipsometry. The second part shows the operation of an ellipsometer, which works on a different principle than the one used in the experiment. The ellipsometer used in the experiment is based on the principle of Null-Ellipsometry.

2.4 Atomic Force Microscopy

Atomic force microscopy (AFM) is a method to determine surface properties. The basic setup is shown in Fig. 2.

A tip ($r < 10$ nm) is scanned over the surface and an image is generated based on the interactions between the sample and the tip. The maximum resolution can be a few Ångströms. In this experiment the measurements are performed in tapping mode (pages 1 - 9 of source [5] and pages 1 - 7 of source [6]). The measurement range within a force-distance curve is shown in Fig. 3.

The following video shows the principle functionality of an AFM: <https://www.youtube.com/watch?v=fivhcWYEtkQ>

3 Procedure

3.1 Safety aspects

Before the experiment day, inform yourself about the dangers of the chemicals listed in Table 3.1.

Also, learn about the handling and risks associated with class 1M and class 3R lasers. Remove rings and other jewellery during the experiment. During the measurements only blackened tools and Laser safety glasses are appropriated. Short pants and open-toed shoes must be avoided, and long hair must be worn closed. Furthermore, the wearing of contact lenses in the laboratory is not allowed.

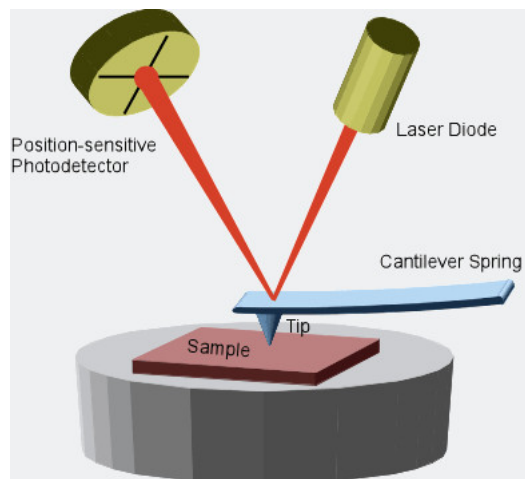


Fig. 2: Scheme of an atomic force microscopy: The tip attached to a cantilever interacts with the sample. A Laser is reflected at the back of the cantilever towards a photodiode measure the forces acting on the cantilever. An image can be generated from this. Taken from: <https://physik.uni-greifswald.de/en/soft-matter-and-biophysics-prof-christiane-helm/methods/afm-atomic-force-microscope/><https://physik.uni-greifswald.de/en/soft-matter-and-biophysics-prof-christiane-helm/methods/afm-atomic-force-microscope/><https://physik.uni-greifswald.de/en/soft-matter-and-biophysics-prof-christiane-helm/methods/afm-atomic-force-microscope/>

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Chemical	Features	Hazard symbols
Silicon	100 Crystal p doping boron	
Toluol	99 %	
Ethanol	≥ 99,8 %	
Polystyrene	$M_w \simeq 192,000$ g/mol	

3.2 Sample Preparation

Cut silicon substrates of dimensions $2 \times 2 \text{ cm}^2$ using a glass cutter. Then rinse the substrates with MQ-Water and clean them for 5 minutes in ethanol in an ultrasonic bath.

Provide a polystyrene solution with 100 g/L concentration. Prepare 10 mL of each of the following concentrations respectively: 5 g/L, 10 g/L, 15 g/L, 20 g/L and 25 g/L. Consider a suitable dilution series in preparation experiment.

The cleaned and dried silicon wafers are coated with polystyrene by means of spin coating. For this purpose, place the wafers in the center of the holder and wet it completely with the respective solution. The rotational speed is 2000 rpm and the coating time is 30 s. To determine the coating thickness in dependence of the rotation speed, two additional test carries should be coated with the 15 g/L solutions at the following rotations: 1000 rpm, 1000 rpm and 3000 rpm.

The rotational speed is 2000 rpm and the coating time is 30s. To determine the dependence of the coating thickness on the rotation speed, two additional test carriers are also coated with the 15 g/L solution at

3.3 Ellipsometry

Switch on the power source on the laser, polarizer and analyzer for the measurement. Use the *Multi70* software and select the *Alignment*. Set the *Angle of incidence* to 70° and place the sample in the center of the stage on the laser spot.

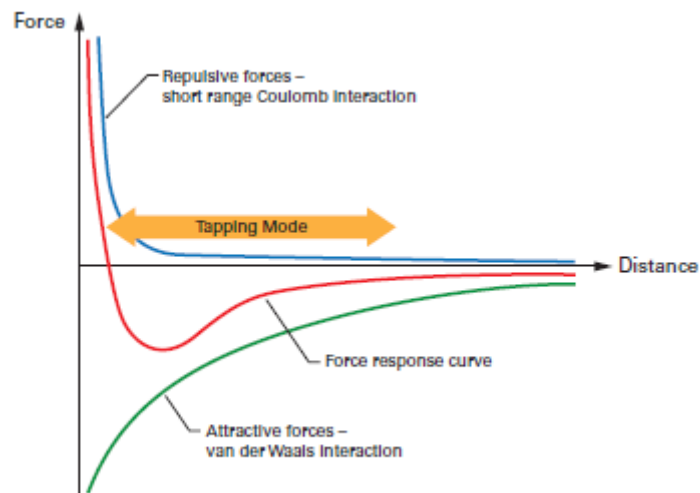


Fig. 3: Force-distance curve: Description of the interaction between tip and sample. Taken from <https://www.bruker.com/products/surface-and-dimensional-analysis/atomic-force-microscopes/afm-application-notes/an133-introduction-to-brukers-scanasyst-and-peakforce-tapping.html>

For optimal results, the sample must be aligned. For this purpose, remove the detector and replace the tube with crosshairs. Open the shutter, then the reflection of the Laser beam is observed. The specimen stage can be moved in height as well as tilted in the plane. The specimen is optimally aligned when the reflected Laser beam can be seen centered on the crosshairs. The periscope is replaced by the detector.

For fine alignment, select the *Sample alignment* menu item in the software. Open the shutter. Now two rings are visible on the screen. These indicate the detector position and the position of the laser beam. Optimized results are achieved when both rings are as well aligned as possible on top of each other. For this purpose, adjust the slope of the sample stage again.

Close the menu item and select *Ellipsometry*. Set the subitem *Algorithm* to *Zone 1/3* and select *Find null setting*. For a given compensator $C = -45^\circ$, the conditions for null ellipsometry are fulfilled for two polarizer and analyzer settings (Zone 1 and Zone 3). The program minimizes the Laser intensity on the detector by rotating the analyzer and polarizer. Then use the *Measure* command to start the measurement, measuring in both Zone 1 and Zone 3. Then the two values Δ and Ψ can be noted, provided that the two polarizer angles from zone 1 and 3 are about 90° and that of the analyzer about 180° difference. If this is not the case, repeat the measurement and readjusted the laser. Close the shutter, move the sample, open the shutter again and measure the next point on the sample.

If possible, measure one point in the center of the specimen and the other 4 at the edge of the specimen and note the respective position of each. When measure the specimen completely, close the shutter and select the *Elli* program. Check if the settings of angle and wavelength are correct for your experiment and load the model *Praktikum* from the path $C:\text{MultiAlt}\backslash\text{Praktikum}\backslash\text{via Load layer model}$. In the *Simulation Parameter* section, the theoretical values can be determined. Take care that the expected measured values are within the limits. By the menu item *Multi* the last 30 measured values can be read from the measuring program. Select the data set to be fitted from the table.3.1. Via the menu item *Fit data set* your data set is fitted to the model.

Make a note of the layer thickness t and the refractive index n . Pay attention to the deviation of measured data and fit data are $\Delta - \Delta^\circ$ and $\Psi - \Psi^\circ$. If the deviations are greater than $0,01^\circ$, check your measurement data and fits and eliminate possible sources of error. If the sample is completely analyzed, the next sample can be placed on the sample table. Now you can start directly with the fine alignment via the menu *Alignment* and the menu item *Sample alignment* in the software.

All samples are measured as described above. The measurement data and fit data are recorded.

3.4 Atomic Force Microscopy (AFM)

Now 3 samples selected by the user are measured, which were previously measured at at least at 5 points by ellipsometry.

To position the specimen in the instrument, first remove the measuring head and place it upside down next to the instrument. Center the specimen on a slide and place on the silver scanner plate. Fix the slide with 2 magnets and don't protrude beyond the scanner stage. Then it is ensured that the spacers (legs) on the measuring head are extended to the maximum. The measuring head is positioned above the sample. Use the bubble level to ensure that the measuring head is in balance during the entire alignment. Switch the external light source on and open the *Asylum Research* program. Select *Standard* → *topography* → *AC Air topography* in the menu.

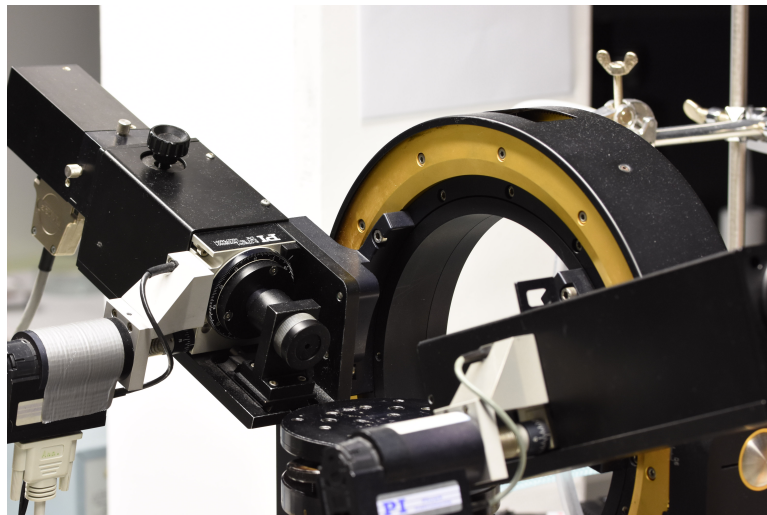


Fig. 4: Ellipsometer Multiscope from Optrel

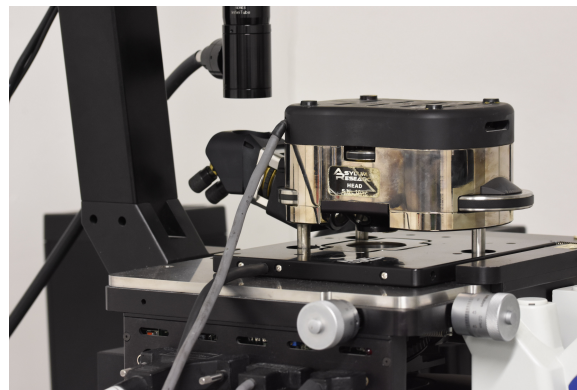


Fig. 5: Atomic force microscope MFP-3D of the company Asylum Research

Open various windows and switch a live view of the spring beam (cantilever) on via the *Video Window* button. At the end of the measuring head (see Fig.6) the focus camera is positioned so that the cantilever is centred and sharp in the image. The *LDX* and *LDY* wheels on the measuring head change the laser position. The laser is positioned in the center of the front part of the cantilever so that the *SUM* value in the *Sum and Deflection meter* panel is maximized. It should be at least 6 V. With the wheel *PD*, adjust the value *Deflection* to zero in order to position the reflection of the laser centrally on the detector. Then determine the resonance frequency and the spring constant of the cantilever.

To do this, switch the light source off and the *GetReal Probe Panel* function is selected in the *Thermal* tab of the *Master Panel*. Select the correct cantilever (AC-160 TS) and start the calibration. After the calibration is finished, the values appear in the *Master Panel*. Now set the excitation of the cantilever. To do this, select the *auto tune* button in the *Tune* tab. Set the oscillation of the cantilever how the free amplitude is 1 V and the cantilever oscillates in 90° phase shift to the excitation?!(Second part). Turn on the light source again and set the following measurement parameters in the *Image* tab: Scan size $10 \times 10 \mu\text{m}$, Points & Lines 256, ScanRate 1 Hz, Setpoint 800 mV and Integral Gain 20. Furthermore, an image name and the storage location (D:\Results\Praktikum\Semester\Gruppenname) are defined under *Path*. Now move the cantilever on the sample.

ATTENTION: If the cantilever is lowered down too far, there is a risk that it will be destroyed. Therefore, special care is required here. Ensure that the measuring head remains in balance. In the panel *Sum and Deflection Meter* the option *Engage* is selected. The piezo crystal is now moved downwards to the maximum. The measuring head is now moved downwards with the corresponding wheels until the cantilever interacts with the sample. The measuring head is moved further down until the display shows *Z Voltage* value around 70 mV. The piezo crystal is now in a middle position and can measure the maximum height difference. With the button *Frame up/down* the measurement can be started. In the *Height retrace* window the surface scan can be followed. The red and blue lines should lie on top of each other to achieve a good image quality. Image optimizations are performed together with the assistant.



Fig. 6: Top view of the measuring head

After the measurement, remove the measuring head from the sample with the corresponding wheels (pay attention to the correct direction of rotation!) and finally remove it from the device. Change the sample and set the measurement parameters to the initial settings again. A new calibration is not necessary. However, check amplitude and phase. If there are strong deviations, position the Laser correctly and tune the cantilever again. Otherwise, move the cantilever directly to the specimen again.

Finally, determine the roughness of the individual samples. For this purpose, select the corresponding image via *AFM Analysis* and call the *Browse saved data*. First, process the image via the *M (Modify)* button. In the tab *Planefit* the sample can be compensated. Further, discuss possible processing steps with the assistant. Determine the root mean square (RMS) on three $1 \times 1 \mu\text{m}$ areas of the sample with the button *A (Analyze)* directly. For each value, applies an error of 80 pm. The three values form a corresponding mean value. Note, all determined roughnesses and save an image file for each sample.

4 Analysis

Summarize your experimental procedure and, in particular, address any deviations from the script. Report your measured values in tabular form and in a suitable graphical representation. Determine the exponents a and b of 10, to establish a relationship of the film thickness d with the angular velocity ω and the concentration c .

$$d \propto \omega^a \propto c^b \quad (10)$$

Compare these with theoretical models and discuss any discrepancies. Also discuss the measured values determined from the Ellipsometry for the refractive index. Determine the roughness of the samples measured by ellipsometry. This can be determined directly from the standard deviation of the layer thicknesses for each sample. Compare the values with those obtained from AFM measurements in terms of accuracy and reproducibility. Also describe the surface topographies from the AFM measurements.

Also, deal with the correct representation of an experimental protocol. This includes formal conventions. You can use the FP Gedankenstutze as a guide: https://www.ipkm.tu-darmstadt.de/media/ipkm/studium_ipkm/f_praktikum/fprakt/Gedankenstuetze_FPProtokoll.pdf.

5 Litterateur

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