HUMBOLDT-UNIVERSITÄT ZU BERLIN

Advanced lab course

Spin coating of thin polymer film and thickness determination by ellipsometry

Topic

It is the aim of this experiment to become familiar with the spin coating technique to prepare thin polymer films and ellipsometry as a tool for thickness determination. Several films of polystyerene on Si/SiO_2 substrates are prepared by spin coating from organic solvents. The thickness is in the range of some ten to hundred nanometers. The film thickness is measured by means of ellipsometry using a commercial instrument. The students should become familiar with the principles polarization optics and reflection.

Keywords

Spin coating, refractive index, Snellius law, Brewster angle, polarization, polarizer

Tasks:

1. Familiarize with the ellipsometer. Try to understand the optical components along the light path and their influence on the polarization of the light.
2. Measure the reflectivity of water for s- and p- polarized light for angles between 45^0 and 70^0. Determine the Brewster angle of water and derive the refractive index.
3. Determine the refractive index of water using ellisometry at angles of 45,50,60, and 65 dgrees
4. Measure the thickness of SiO_2 on Si for three samples. It is necessary to measure at three different sites on every sample!
5. Spin coat poly styrene from given solution on silicon substrates with different rotation speeds. The speeds can be varied between 10 and 80 s^{-1}. You should spin coat samples in steps of 10 s^{-1}
6. Spin coat 5 samples with a speed of 50 s^{-1}.
7. Measure the thicknesses of the poly styrene samples.
8. Fit the thickness of the SiO_2 layer for the substrates using a respective two-layer model.
9. Fit the thickness of the polymer layer for the samples using a respective three-layer model.
10. Calculate the average thickness and maximum error for the five samples of task 5. This error gives you an errorbar for the other samples of task 4.
11. Plot the film thickness vs. the rotation frequency on a double logarithmic gtraph and derive the exponent that describes the decay.

Introduction

Spin coating is a method to prepare thin and utra thin films of a soluble material on a solid substrate. The material is spread on a disk-like substrate and under rotation it is partially removed by centrifucgal forces to form a homogeneous film. The film is thinning further by evaporation of the solvent to achieve a final thickness. This method is very wide spread in industry, especially to prepare films of photo-resists on semiconductor wafers.
Ellipsometry is an elegant method to measure thickness of thin films of optical transparent materials. It is based on the effect, that the state of polarization changes when light is reflected at an interface. The technique allows measurement of complex refractive index of a homogeneous material as well as thickness of a film. In the latter case, multiple reflection between the internal interfaces have to be taken ijnto account for the evaluation of the reflection amplitudes.
In the following chapter a brief introduction into the techniques and theory is given.

Spin coating

The process of spin coating is best decribed as a multi-step process, see Figure 1. First, the solution is deposited on the substrate (Deposition) and rotation is started with certain acceleration (Spin-Up). Due to centrifugal forces the liquid is spun horicontally and homogeneously distributed over the substrate. The film thickness reduces due to loss of material. In parallel, the viscosity of the material increases due to evaporation of solvent which will stop the horizontal flow of liquid (Spin-Off). Afterwards, the thickness reduces only slowly due to evaporation of solvent (Evaporation).
An exact mathematical treatment of this process is difficult and only possible under certain simplifying assumptions or by heavy numerical simulation. One can show however, that the resulting film thickness h_f depends mostly on the viscosity of the solvent η and the spin frequency ω by the following relation:
[Ems58, Hall98].

$$h_f \propto \eta^{1/3}\omega^{-\alpha} \qquad (1)$$

The exponent α varies between 1/2 and 2/3 depending on the speed of evaporation in comparison to the speed of thinning due to horizontal flow.

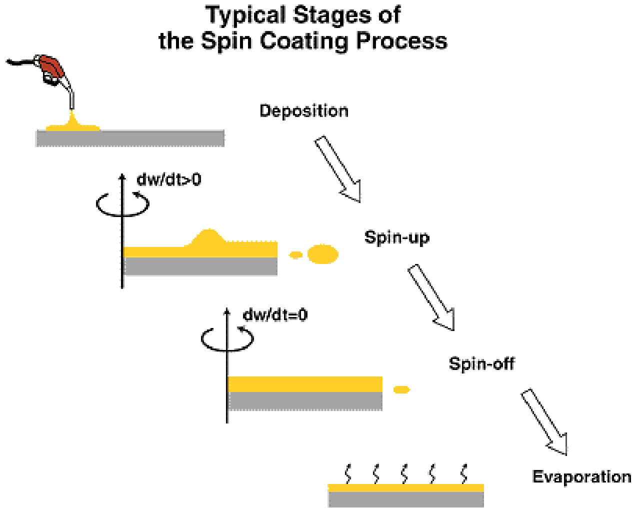

Figure 1: Schematical view oft he spin coating process (taken from http://www.brewerscience.com/research/processing-theory/spin-coater-theory/ and http://www.semiconductor.net/article/203104-How_to_Minimize_Resist_Usage_During_Spin_Coating.php

Theory of Ellipsometry

Polarized light

Ellipsometry measures the change oft he polarization of light upon reflection at a surface. This change of polarization is related to the refractive index of the optical properties of the sample where light is reflected. In case that there is a transparent film with thickness *d* on a substrate, the polarisation is highly affected by the film. Hence, ellipsometry provide a means to measure film thicknesses in the range of a few Angstrom up to several hundred nanometers.
In order to understand the formalism that is used to evaluate quantitatively thicknesses and reefrctive indices one needs first to understand the properties of light.

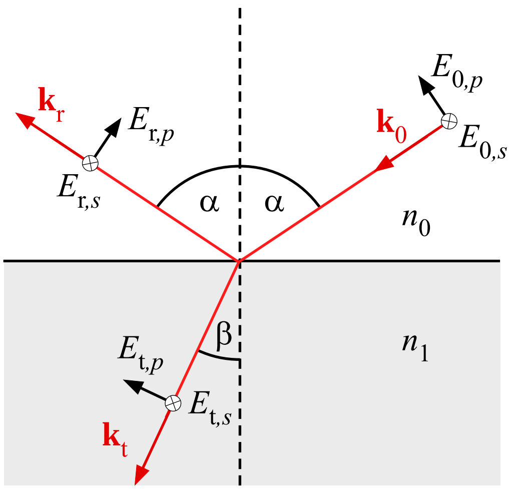

Figure 2: plane of incidence with directions of incident, reflected, and transmitted waves and their respective base vectors to describe state of polarization.

Light is described by a plane wave of an electric field vector **E** and the optical properties of any materials envolved are described by refractive indices n. The wave is travelling along the wave vector **k**, where **E⊥k.** In kartesian coordinates, the plane wave of the electric field **E**at position **x** is described by the relation

$$\mathbf{E} = \mathbf{E_0}\, e^{(-i(\mathbf{kx}-\omega t))}, \tag{1}$$

where $k = 2\pi/\lambda$ is the wave vector and ω the frequency. For many applications (also here!) it is more favorable to describe the polarization within a plane wave perpendicular to the k-vector. The direction of polarization is then given by the linear combination of two base vectors, one perpendicular to the plane of incidence, the s-component E_s, and one in parallel to the plane of incidence, the p-component E_p. Since the E-vector is not a static component but it is oscillating with time, the phase δ between these base vectors is another important characteristic. These properties are summarized using a 2-dimensional complex vector, the so called Jones vector:

$$\mathbf{E} = \begin{pmatrix} |E_p| e^{i\delta_p} \\ |E_s| e^{i\delta_s} \end{pmatrix} = \begin{pmatrix} E_p \\ E_s \end{pmatrix}. \tag{2}$$

The state of polarization is then characterized by the phase difference $\delta_p - \delta_s$.

Three special cases of polarization can be considered:

a) Linear, for $\delta_p - \delta_s = 0$ or $\delta_p - \delta_s = \pi$,
b) Circular, for $\delta_p - \delta_s = \pi/2$ and $|E_p| = |E_s|$,
c) Elliptic, for $\delta_p - \delta_s \neq 0$ and $|E_p| \neq |E_s|$.

Short theory of reflection

If light is reflected at a surface, the state of polarization changes. This change is characteristic for the properties of the surface. We describe the change of polarization by the Jones vectors, because they are independent of the direction of the light, i.e. the direction of the base vectors does not change upon reflection or transmission. Only the amplitude and phase of the respective components are altered. Therefore, we write for the amplitudes of the incident and the reflected light beam:

$$\mathbf{E_i} = \begin{pmatrix} |E_p^{\mathrm{r}}| e^{i\delta_p^{\mathrm{r}}} \\ |E_s^{\mathrm{r}}| e^{i\delta_s^{\mathrm{r}}} \end{pmatrix}, \qquad \mathbf{E_r} = \begin{pmatrix} |E_p^{\mathrm{r}}| e^{i\delta_p^{\mathrm{r}}} \\ |E_s^{\mathrm{r}}| e^{i\delta_s^{\mathrm{r}}} \end{pmatrix}. \tag{3}$$

On the other hand, the reflection is described by the Fresnel coefficient r_p and r_s, which describes the change of the respective amplitude and phase:

$$\boldsymbol{r_p} = \frac{|E_p^{\mathrm{r}}|}{|E_p^{\mathrm{i}}|} e^{i(\delta_p^{\mathrm{r}} - \delta_p^{\mathrm{i}})}, \quad \boldsymbol{r_s} = \frac{|E_s^{\mathrm{r}}|}{|E_s^{\mathrm{i}}|} e^{i(\delta_s^{\mathrm{r}} - \delta_s^{\mathrm{i}})} \tag{4}$$

Note that these coefficients are complex numbers. The ratio between these two coefficients can be expressed by two angles using the relation

$$\tan \Psi \cdot e^{i\Delta} = \frac{r_p}{r_s}, \tag{5}$$

$$\tan \Psi = \frac{|E_p^{\mathrm{r}}|/|E_p^{\mathrm{i}}|}{|E_s^{\mathrm{r}}|/|E_s^{\mathrm{i}}|} \tag{6}$$

$$\Delta = (\delta_p^{\mathrm{r}} - \delta_s^{\mathrm{r}}) - (\delta_p^{\mathrm{i}} - \delta_s^{\mathrm{i}}). \tag{7}$$

Equation (5) ist the so called „Ellipsometry equation“, because it is the master equation for our method. Using so called “*Null Ellipsometry*”, these angles can directly be read out from the instruments (see below).

For a plane surface, the coefficients are simply given by the *Fresnel coefficients* which depend on the angle of incidence α and the refractive index n of the substrate material.
In case that there is a thin film on the surface, the reflection coefficients also contain information about the thickness of the film. This can be calculated by following a light beam as it is reflected and transmitted at the substrate/film and film/air interface infinite times, as indicated in Figure 3. The system is modeled in this case by 3 “layers”: the air, with refractive index $n_0 = 1$ and infinite thickness, the film with thickness d and refractive index n_1, and the substrate with refractive index n_2 and again infinite thickness.

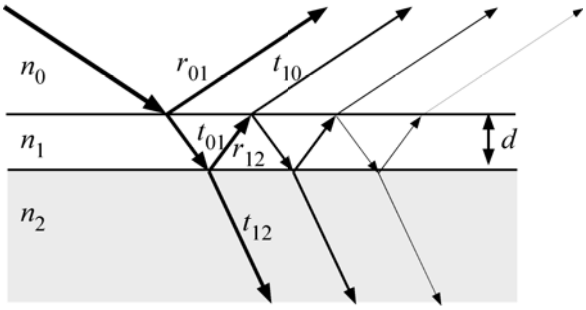

Figure 3: Multiple reflection of light beam within a thin film.

Summing up all parts that are reflected, on obtains a geometrical series which can be evaluated mathematically. The result for the reflection coefficients is then

$$r_p = \frac{r_{01,p}+r_{12,p}e^{-i2\beta}}{1+r_{01,p}r_{12,p}e^{-2i\beta}} \tag{9}$$

$$r_s = \frac{r_{01,s}+r_{12,s}e^{-i2\beta}}{1+r_{01,s}r_{12,s}e^{-2i\beta}} \tag{10}$$

where the coefficients $r_{01,s}$, $r_{01,p}$, $r_{12,s}$ und $r_{12,p}$, describe reflexion at the respective interfaces between medium with n_0 and n_1 and between n_1 and n_2 . It is calculated for p- and s-polarized light seperately. The thickness and the angle of incidence are contained within the phase factor given by

$$\beta = 2\pi\frac{d}{\lambda}\sqrt{n_1^2-n_0^2\sin^2\varphi} \tag{11}$$

The thickness is evaluated from the ellipsometric measurement by fitting these formulas. The model above is used to calculate r_s,and r_p, and hence ψ and Δ, then the thickness is adjusted until ψ and Δ agree with the measured values.

For a system with two or more filme of different refractrive indices, the model is expandedby taking into account all reflections and transmission at all films. Again, the thickness of one of the films is fitted numerically to the measured data.

Description of the instrument

The principle of an ellipsometer is sketched in Figure 4. The main components are as follows:

- Polarizer P; is used to create linear polarized light of arbitrary orientation.
- Compensator C; is used to create elliptically polarized light.This component is a $\lambda/4$ plate.
- Sample S.
- Analyzer A; this is a polarizer as P and used to extinguish the reflected light beam.
- Photodetektor D.

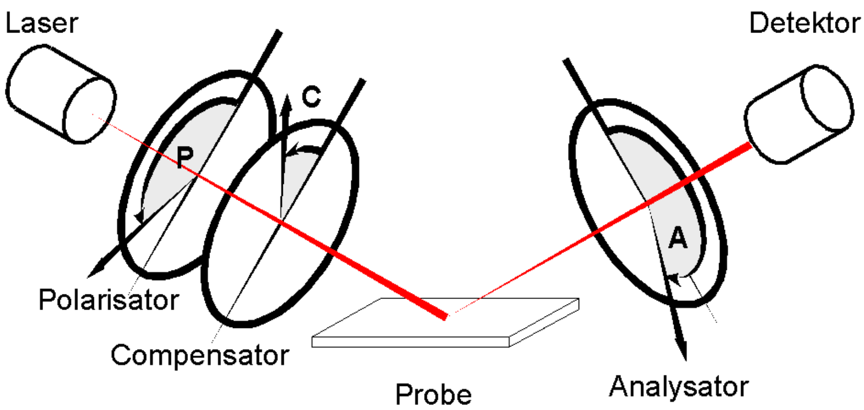

Figure 4: Setup of an ellipsometer. See text for description.

In the mode of *Null Ellipsometry* the polarization of the incident beam is tuned such that the reflected beam is linearly polarized. (Note: for a simple plane surface, the reflected beam is linearly polarized if and only if the incident beam is linearly polarized.) In this case the reflected beam can be eliminated by the analyzer if it is oriented perpendicular to the polarization direction. Therefore the experimental task is: find the position of the polarizer and analyzer where the intensity at the detector is at it's m inimum, in the ideal case equals zero.

The compensator is a λ/4-plate which is rotated by ±45° against the *p*-direction. If one calculates the reflection coefficients for this condition and fort he case that the reflected light is linearly polarized, one finds a very simple relation between the direction oft he polarizer P_0 , the direction of the analyzer A_0 and the angles Ψ and Δ as follows:

$$\tan\Psi\, e^{\iota\Delta} = \tan A_0 \exp\left(i\left(2P_0 + \tfrac{\pi}{2}\right)\right), \quad \text{falls } C = -45^\circ, \qquad (8a)$$

$$\tan\Psi\, e^{\iota\Delta} = -\tan A_0 \exp\left(i\left(\tfrac{\pi}{2} - 2P_0\right)\right), \quad \text{falls } C = 45^\circ. \qquad (8b)$$

For one pair (P_0, A_0), where extinction of reflected light is observed, one finds another pair at ($P_0 + 90^\circ$, $180^\circ - A_0$). These pair are called *ellipsometric zones*. Using two zones one can increase the accuracy oft he ellipsometric measurement.