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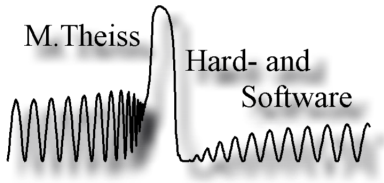

Analysis of optical spectra by computer simulation - from basics to batch mode

by Wolfgang Theiss

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Foreword

This document gives a short summary of several talks and documents about spectrum simulation.
All the pictures are just screen shots, not prepared explicitly for this document. In between the pictures there are comments that should guide you from slide to slide.
Most of the slides in the talks are interactive pictures: You can vary slider positions and see what happens to the spectra. Unfortunately, in this static document these dynamical impressions cannot be reproduced.

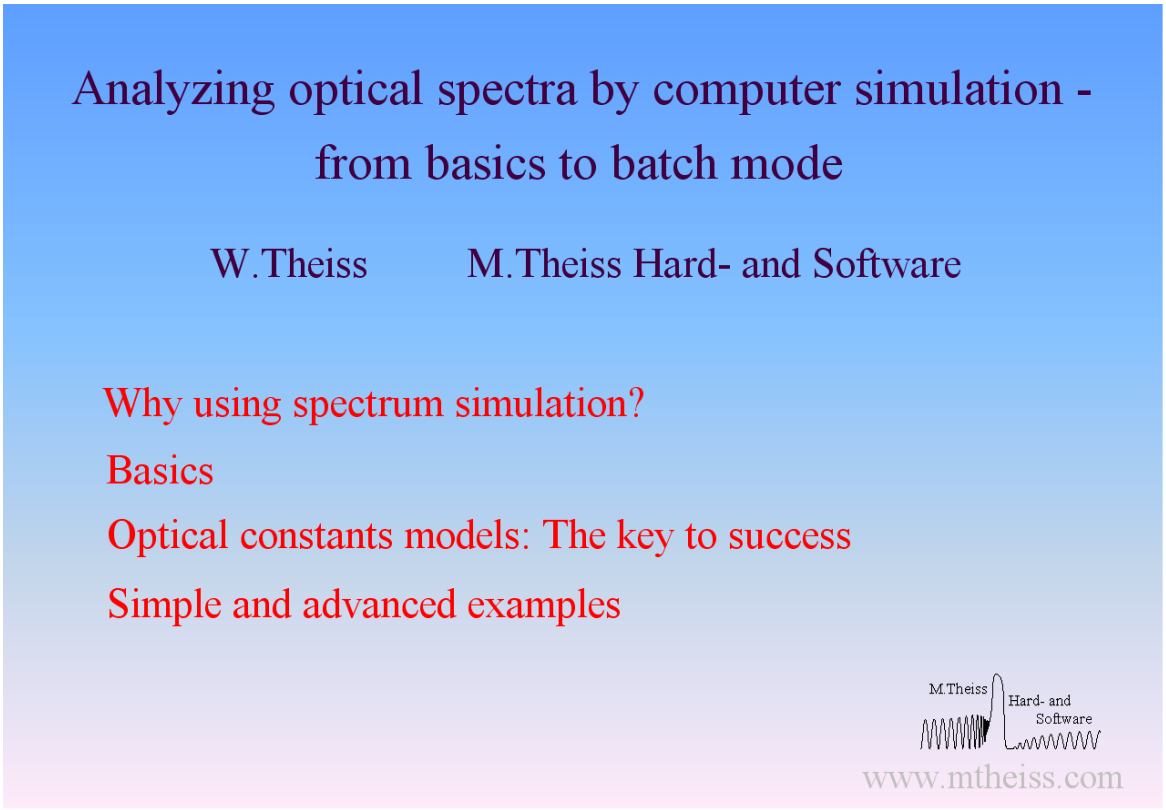
In the graphs displaying optical constants the real part is drawn blue, the imaginary one is given in red.
In the case of spectrum fits, the measured spectra are always in red, the simulated spectra in blue.

All simulations have been performed with our SCOUT software which is commercially available.

Aachen, November 2002

1 Title

Title, author, company and overview:



2 Why using spectrum simulation?

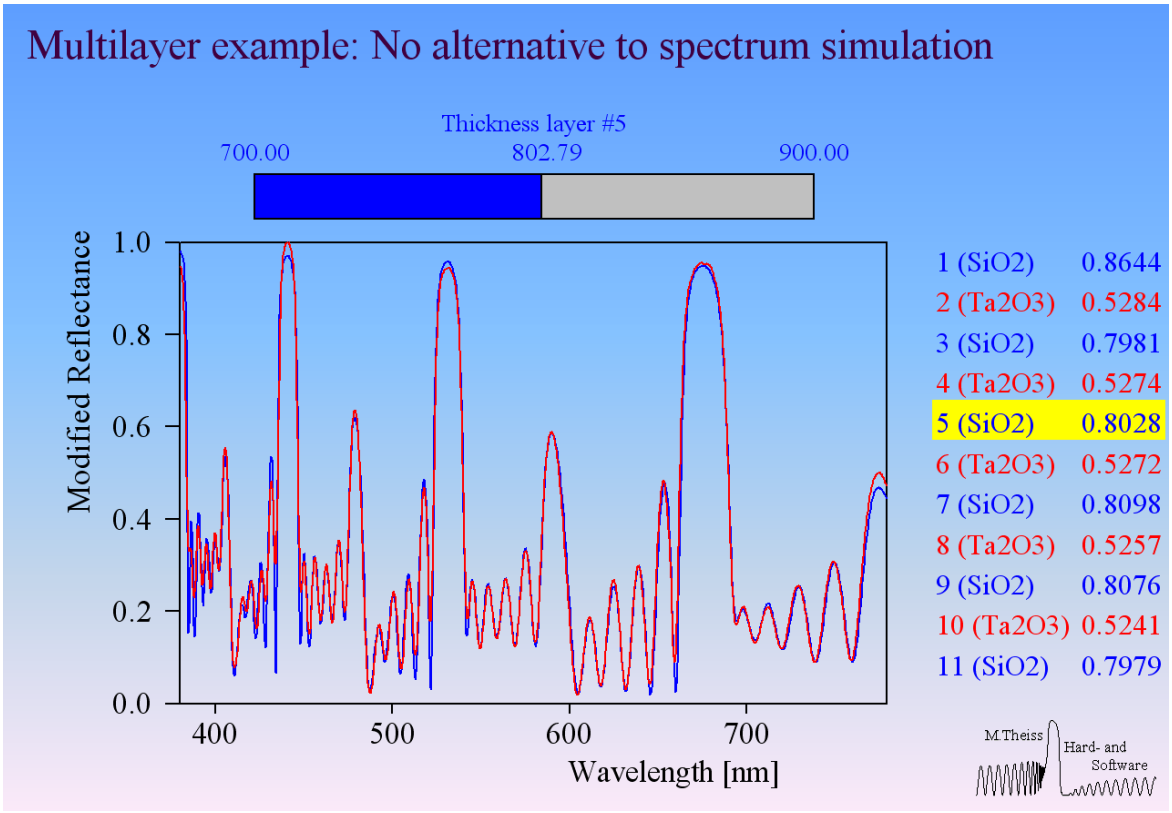
2.1 Overview

Analyzing optical spectra by computer simulation (based on physical models) is a standard method in spectroscopic ellipsometry. In the case of reflectance and transmittance spectroscopy it is not yet well-established. Here are some reasons for applying this method:

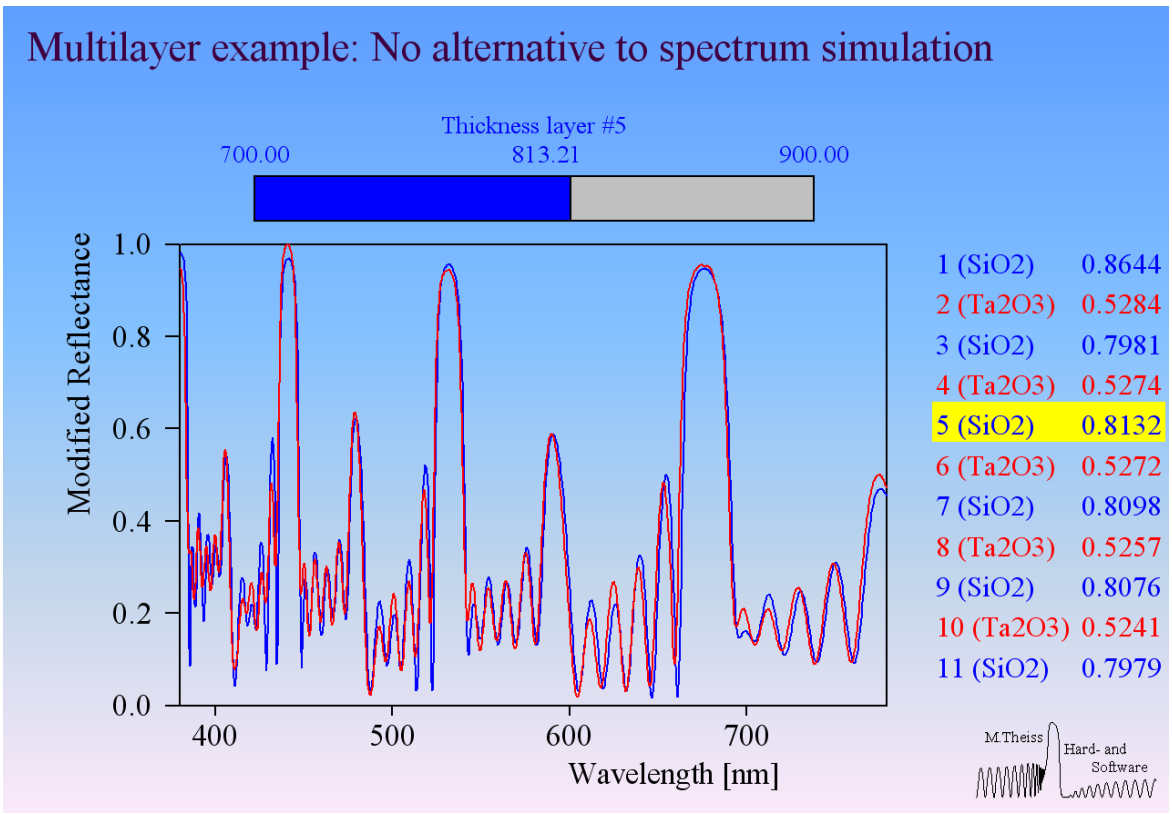
1. In the case of multilayer stacks there is no alternative
2. Simple data analysis procedures are usually based on some crude assumptions which can be avoided using a simulation approach
3. Simulated spectra can be used to check the qualitiy of spectroscopic measurements
4. Spectrum simulation is ideal for teaching optics and spectroscopy
5. Well-working simulations of measured data can be pre-cursors of successful designs of thin film products

2.2 Multilayer stacks - no alternative

In the case of multilayer stacks there is no alternative to spectrum simulation. Only on the basis of a physical model the complicated spectral features can be understood. The example below shows the comparison of the measured (red) and simulated reflectance (blue) of a stack of 11 layers on silicon:



The increase of one of the layer thicknesses (layer 5, marked yellow) by 10 nm leads to complicated variations of the spectrum which can only be handled by a reliable physical model:



2.3 Avoid approximations of simple analytical methods

Simple analytical methods are most often based on simplifying assumptions. Examples of simple evaluation procedures are

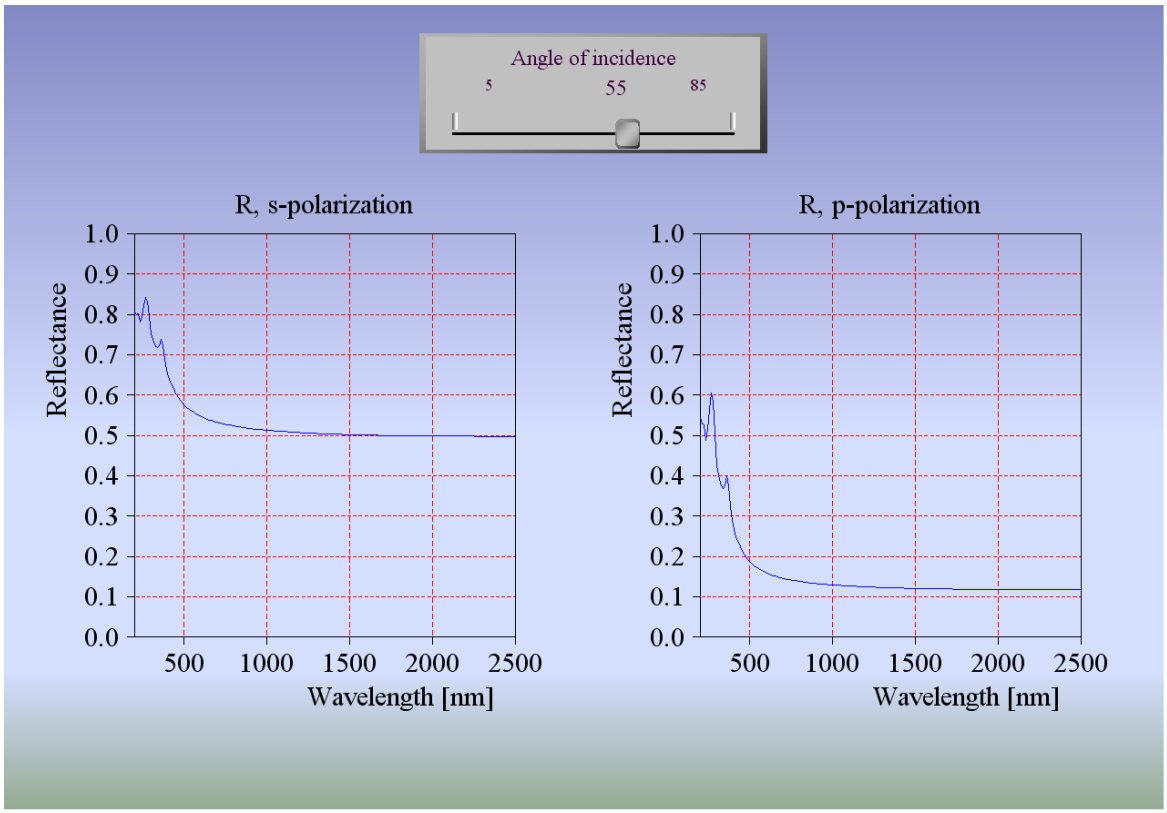
- the conversion of transmittance spectra to absorbance
- the conversion of diffuse reflectance spectra to so-called Kubelka-Munk functions
- thickness analysis of reflectance or transmittance spectra by the Fourier-transform technique
- direct determination of optical constants from reflectance and transmittance measurements in the case of simple geometries

All these methods can be replaced by spectrum simulation which can be applied avoiding most of the simplifying assumptions.

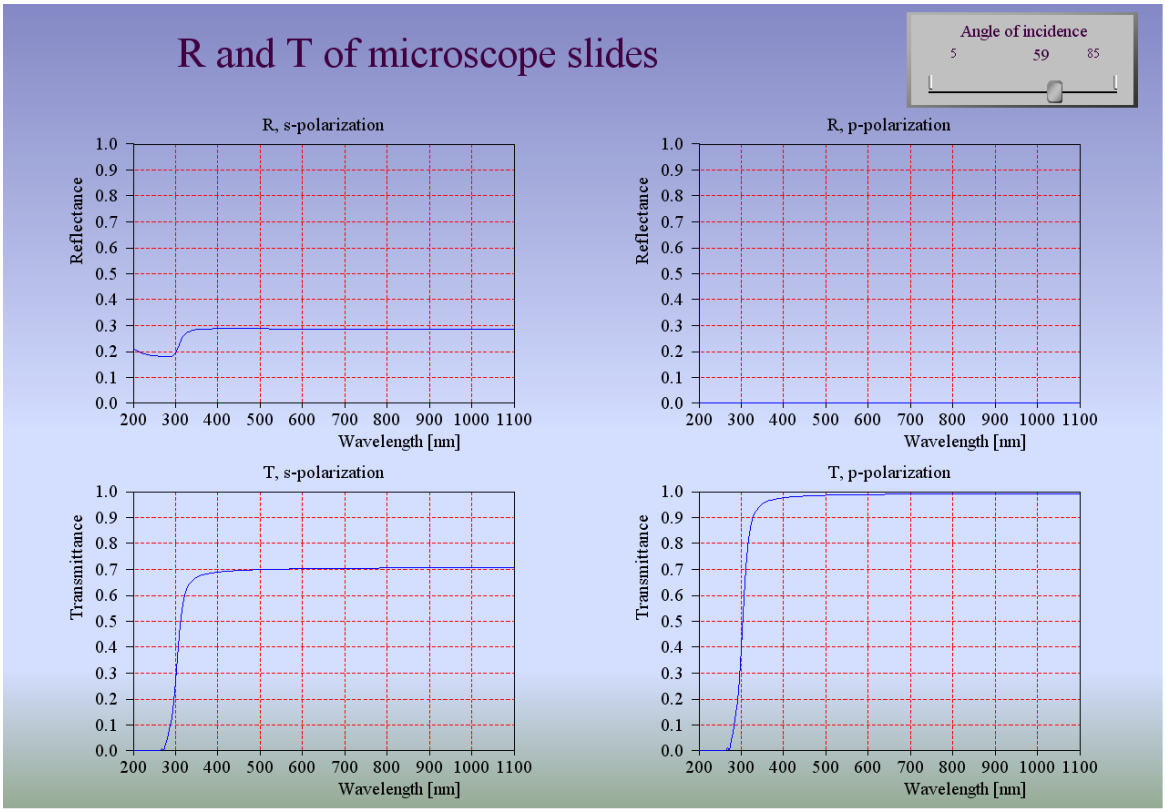
However, spectrum simulation is not as easy as the techniques mentioned above, and the development of a suitable optical model may require some time and experience.

2.4 Use spectrum simulation to check spectrometer hardware

Simulated spectra of well-known and reproducible samples can be used to check the performance of experimental setups.
A quick, simple and very useful test for reflectance accessories is to compare the measured reflectance of a silicon wafer (for a given angle of incidence and polarization) with simulated data. The simulation can be based on literature data for the optical constants of silicon (and the native oxide on top of the wafer):



A similar simple test for correct reflectance and transmittance measurements can be done with conventional microscope slides. The measured spectra should not differ from the simulated ones by more than 1 or 2 percent:



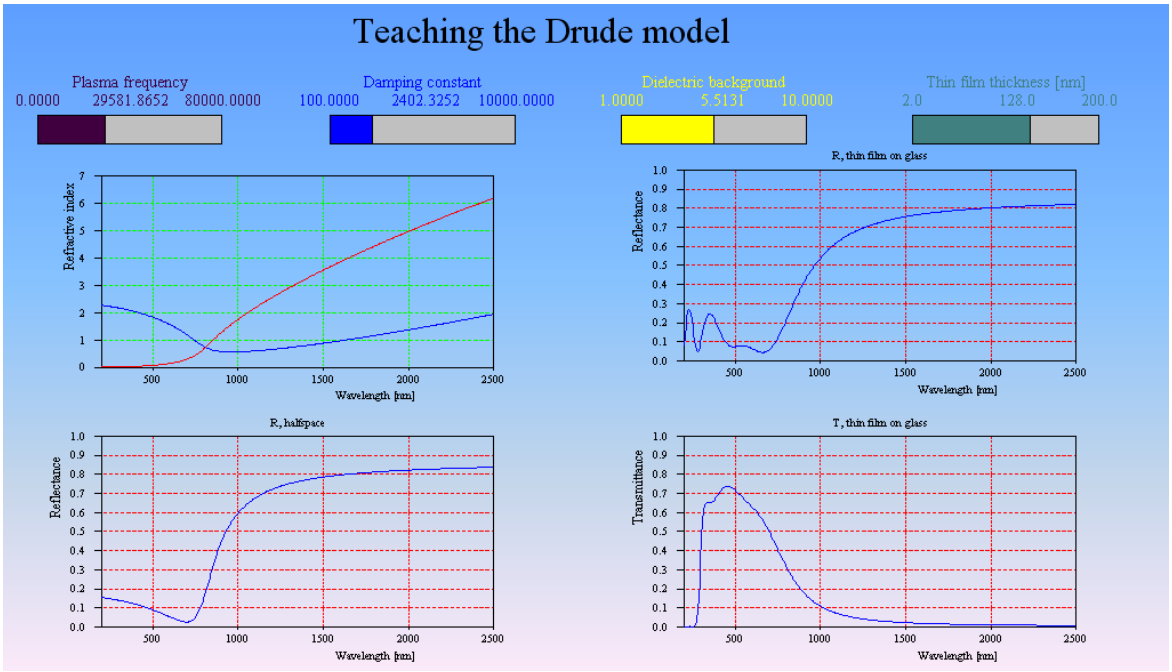
2.5 Spectrum simulation is very educational

Using a spectrum simulation software, you can easily try what happens if you

- change a layer thickness
- use a different substrate
- change the angle of incidence
- work with a polarizer
- add a surface oxide
- ....

All these investigations can be done without any experimental effort and costs.

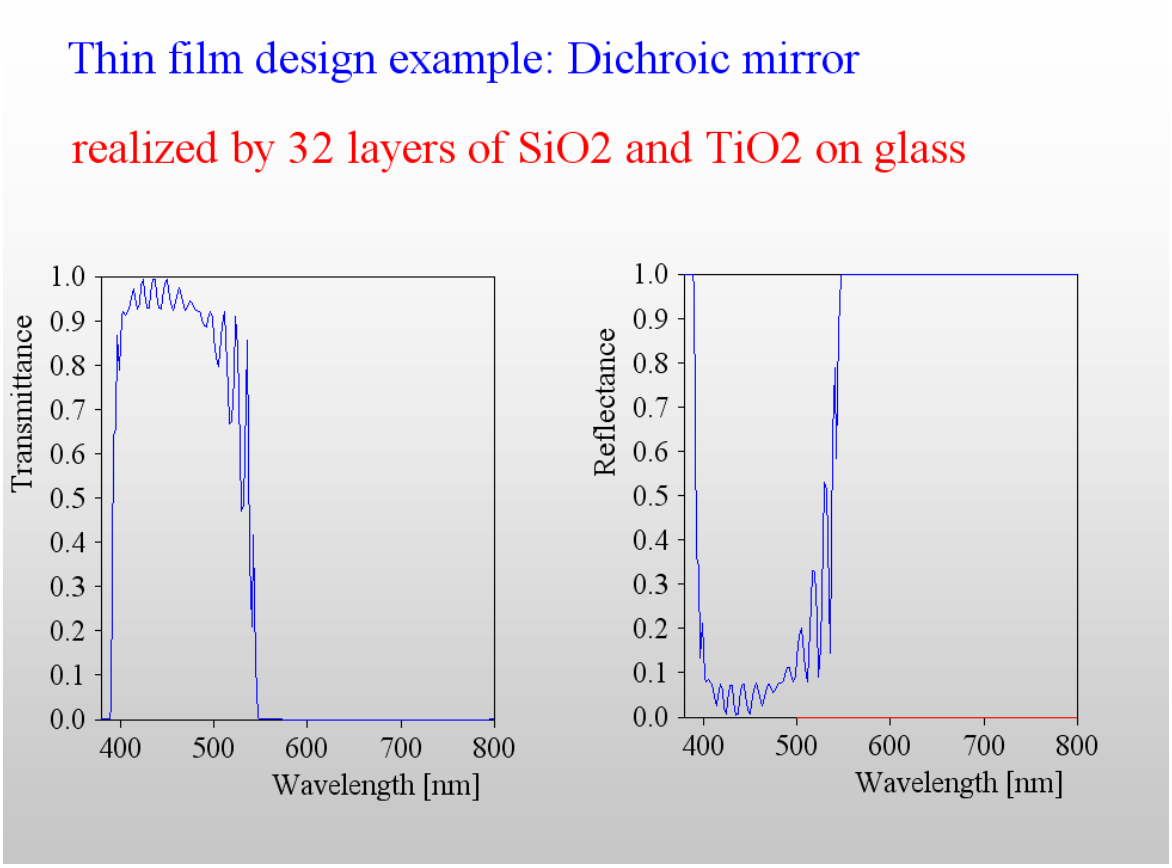
The example below shows how the optical properties of charge carriers (electrons, holes) can be explained by interactive variation of the relevant quantities such as concentration and damping:



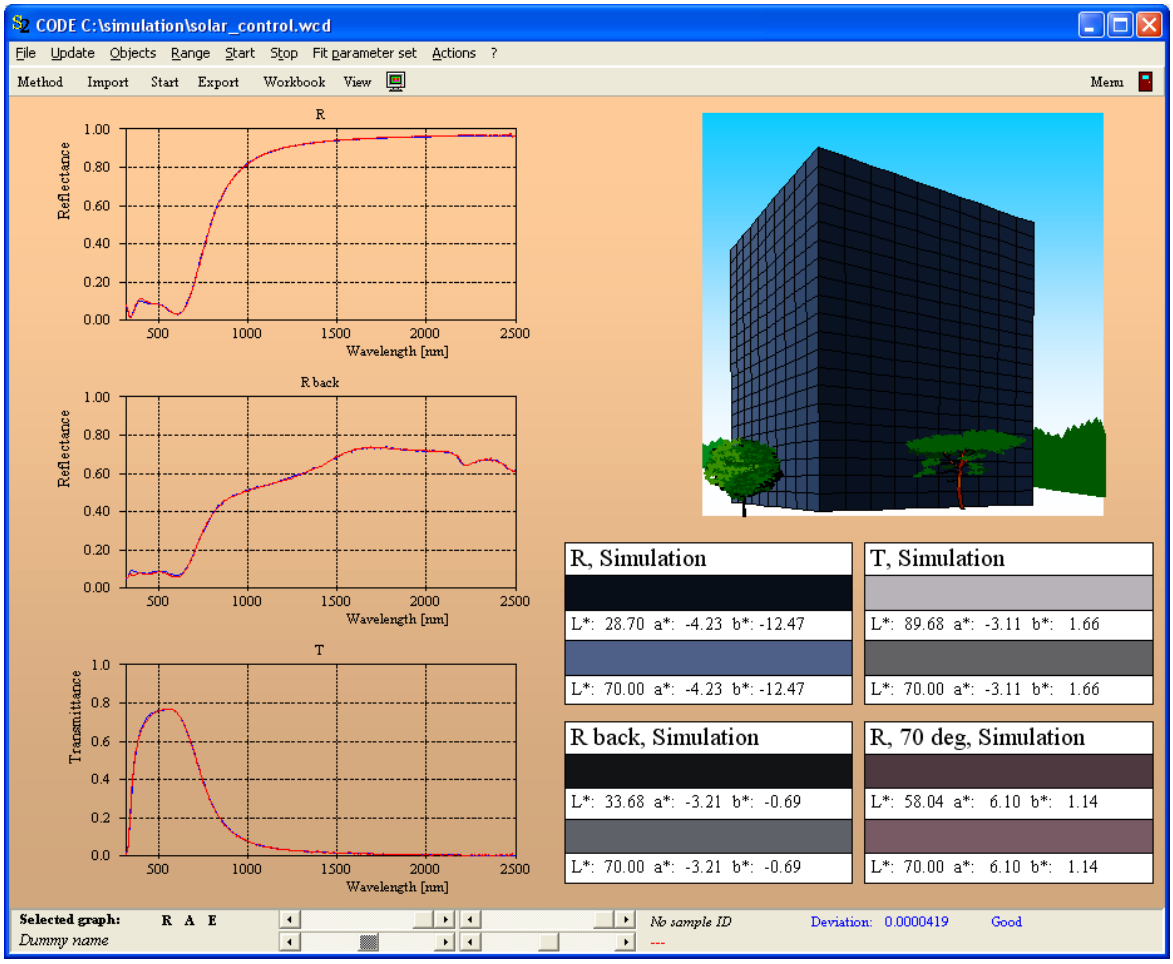
2.6 Spectrum simulation as pre-cursor of thin film design

Successful analysis of measured spectra of single and multiple layers can be pre-cursors of reliable thin film design. If the optical constants of the used materials are known, and if interface effects of multilayers are understood and included in the model, one can predict and design the properties of new thin film products with a minimum of experimental work.
Thin film design is very similar to thin film analysis. First a target function (e.g. a wanted reflectance spectrum, a certain color or an integral transmittance value) is defined. Then some of the model parameters like layer thicknesses are (interactively or automatically) varied until the target is reached.

As an example the transmittance and reflectance spectra (45 deg angle of incidence) of an optical filter (dichroic mirror) is shown below. The task of the layer stack is to separate radiation below and above 550 nm in a color display device (beamer):



Spectrum simulation is widely used to design and optimize architectural glass coatings. Based on good optical constant models for sputtered oxides and metals, the appearance of multilayer coatings on glass panes is predicted with high precision. The example given below shows measured and simulated spectra of a so-called solar control coating and the corresponding colors:



3 Basics of spectrum simulation

3.1 Overview

Analysis of optical spectra by computer simulation is done in 5 steps:

1. Define the optical constants of all materials in the system
2. Setup the layer stacks
3. Define the spectra which are to be computed and compared to measured ones
4. Select the model parameters that are to be varied ('fitted') in order to minimize the difference between simulated and measured spectra
5. Change the model in an interactive or automatic way until the measured data are reproduced with acceptable quality

3.2 Optical constants

Materials appear in Maxwell's equations via the complex dielectric function. The square root of this quantitiy is called the refractive index. Both the refractive index as well as the dielectric function are sometimes called 'Optical constants'.
Each material has a very characteristic frequency dependence of its optical constants. The key to good spectrum simulation results is the right choice of optical constant models. This very important issue will be discussed in a separate section below.

Optical constants

$\varepsilon = \varepsilon' + i\varepsilon''$: Dielectric function

$\chi = \chi' + i\chi''$: Susceptibility

$n + ik$: Refractive index

$$n + i\kappa = \sqrt{\varepsilon(\omega)}$$

How does a material respond to electric fields?

$$\vec{D} = \varepsilon_0 \varepsilon \vec{E},\ \varepsilon = 1 + \sum_i \chi_i \qquad \vec{P} = \varepsilon_0 \chi \vec{E}$$

Propagation of plane waves:

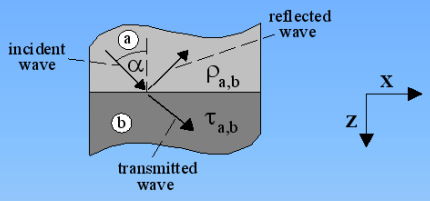
$$\vec{E}(\vec{r},t) = \vec{E}_0 \exp\left(i n \vec{k}_0 \cdot \vec{r} - i\omega t\right) \exp\left(-\kappa \vec{k}_0 \cdot \vec{r}\right) \qquad \left|\vec{k}_0\right| = \frac{2\pi}{\lambda_0}$$

3.3 Layer stacks, wave propagation

Light waves are partially reflected and transmitted at interfaces between two materials with different optical constants. The amplitudes of the reflected and transmitted waves are given by Fresnel's equations:

Reflection and transmission of light at interfaces

Waves at the interface between two layers:



$\rho_{a,b}$: amplitude reflection coefficient

$\tau_{a,b}$: amplitude transmission coefficient

Fresnel equations

s-polarization: $\rho_{ab} = \frac{\tilde{N}_a - \tilde{N}_b}{\tilde{N}_a + \tilde{N}_b}$ $\tau_{ab} = \frac{2\tilde{N}_a}{\tilde{N}_a + \tilde{N}_b}$

p-polarization: $\rho_{ab} = \frac{\tilde{N}_a/\varepsilon_a - \tilde{N}_b/\varepsilon_b}{\tilde{N}_a/\varepsilon_a + \tilde{N}_b/\varepsilon_b}$ $\tau_{ab} = \frac{2\tilde{N}_a/\varepsilon_a}{\tilde{N}_a/\varepsilon_a + \tilde{N}_b/\varepsilon_b}$

Generalized refractive index: $\tilde{N} = \sqrt{\varepsilon(\omega) - n_a^2 \sin^2\alpha}$

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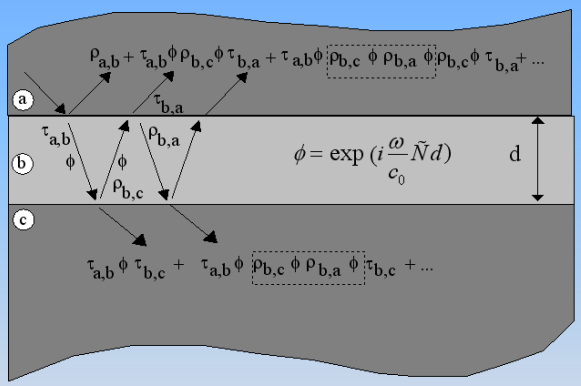
In the case of a single layer between two 'halfspaces' the total reflected and transmitted waves are the sum of many partial waves. The summation can be done conveniently making use of a geometric series:

Reflection and Transmission of a single layer

Taking into account multiple reflections:



amplitude reflection coefficient

$$r_{a,b} = \rho_{a,b} + \frac{\tau_{a,b}\,\phi\,\rho_{b,c}\,\phi\,\tau_{b,a}}{1 - \rho_{b,c}\,\phi\,\rho_{b,a}\,\phi}$$

amplitude transmission coefficient

$$t_{a,b} = \frac{\tau_{a,b}\,\phi\,\tau_{b,c}}{1 - \rho_{b,c}\,\phi\,\rho_{b,a}\,\phi}$$

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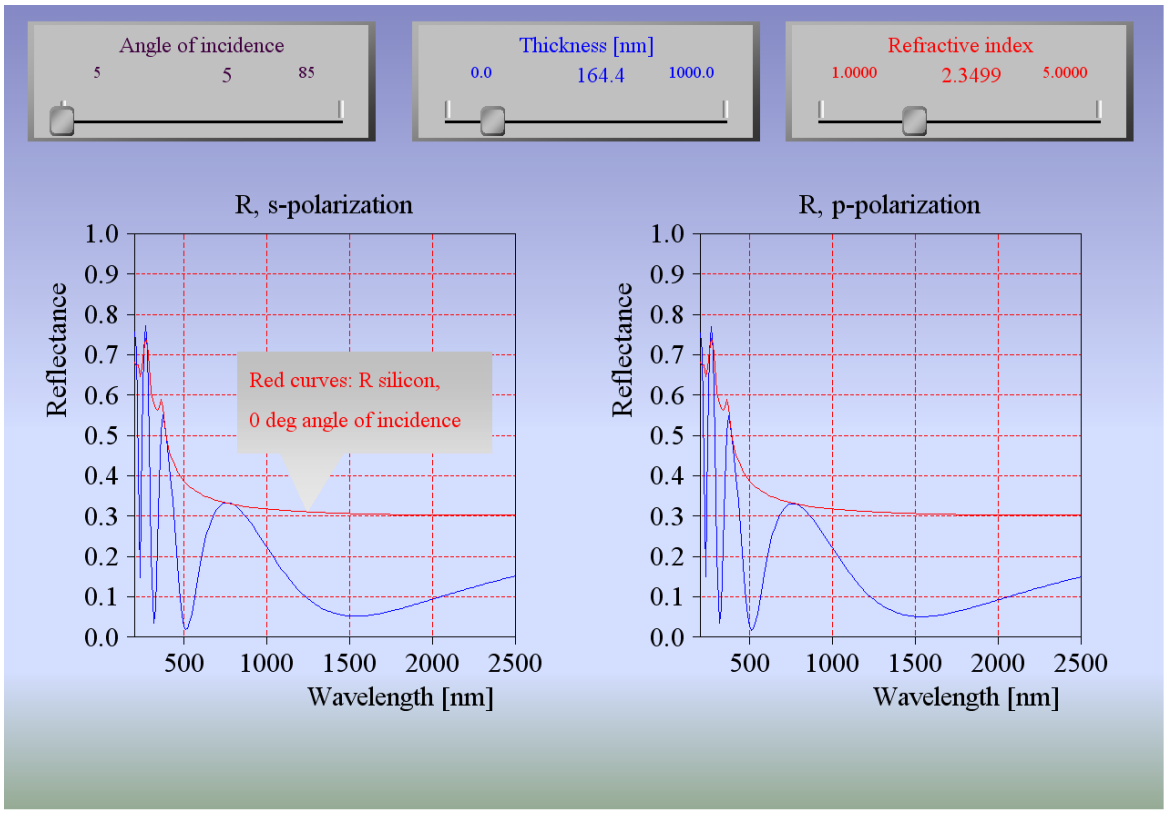
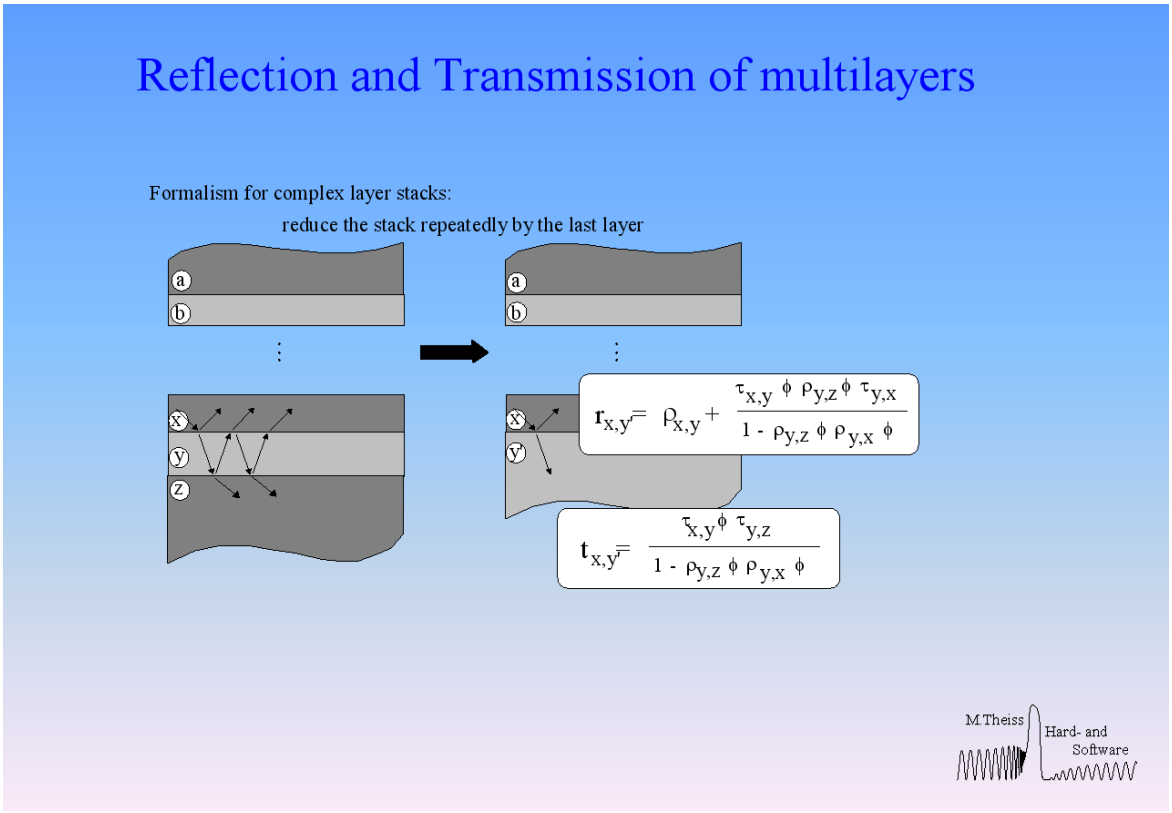
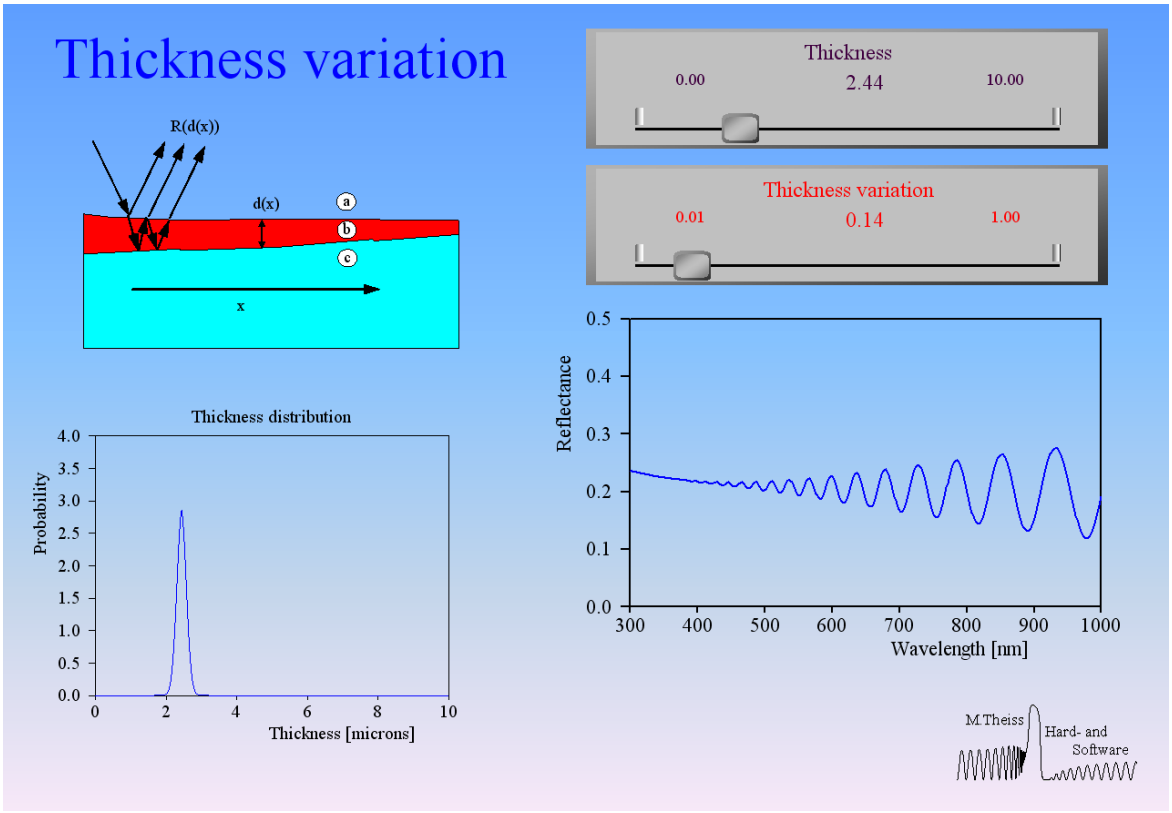
The phase shift ϕ leads to interference fringes in the case of a transparent layer:



The amplitude of the reflected and transmitted wave of a multilayer stack can be computed using a matrix method or by recursively applying the result for a single layer (the geometric series shown above) as sketched below. The 'recursion method' can easily be extended to the case of thick layers (like glass plates) which do not exhibit interference fringes in optical spectra (incoherent superposition).



If the thickness of a layer is not constant within the illuminated sample spot one has to average reflectance values for different values of the thickness. This can be done with low computational effort if the Fourier transform of the thickness distribution can be computed analytically. Here is an example of a Gaussian thickness distribution showing the influence of the thickness averaging to the envelope of the interference pattern:



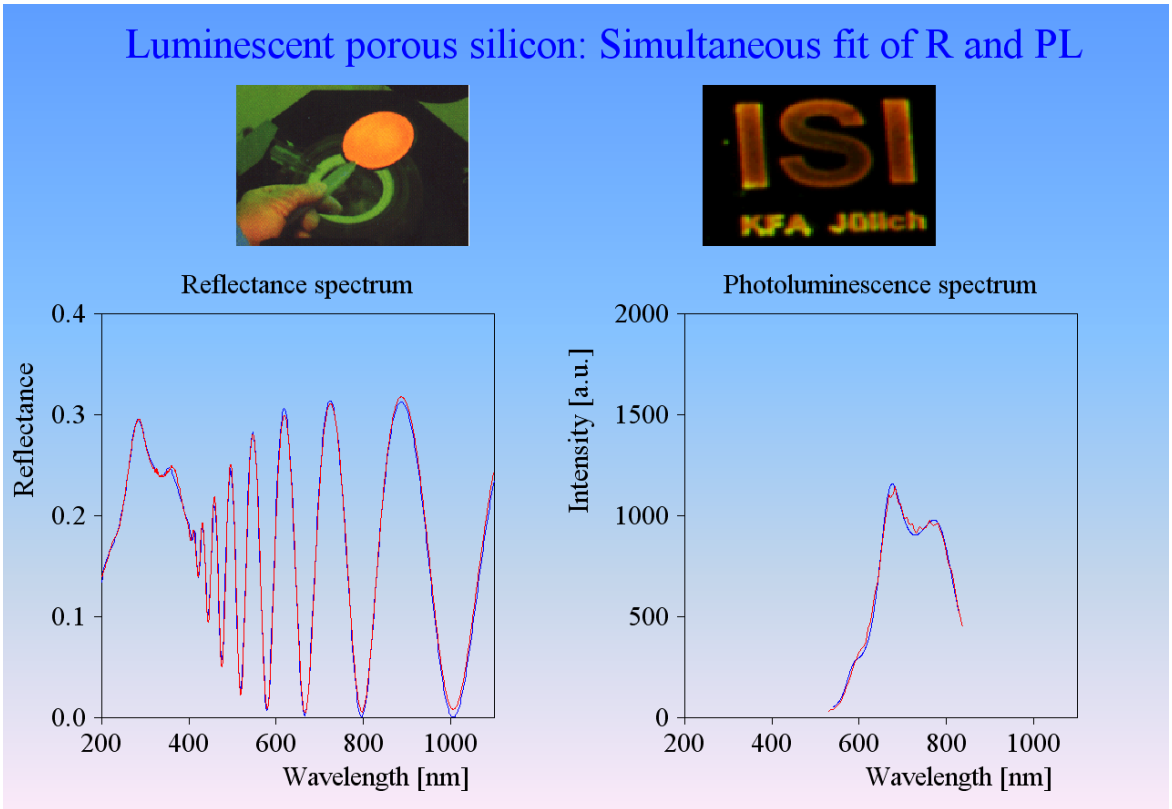
3.4 Spectra

Spectrum simulation can be done easily for

- reflectance
- transmittance
- ellipsometry
- ATR (attenuated total reflection)

at arbitrary angles of incidence and polarization.

The SCOUT software of M.Theiss Hard- and Software also contains a method for the simulation of photoluminescence or fluorescence spectra:



In the case of multiple spectrum fits each spectrum should have an individual weight for the computation of the total fit deviation (i.e. the difference between measured and simulated spectrum).

3.5 Parameter fitting

The last steps of spectrum analysis by computer simulation are the selection and adjustment of those model parameters which are to be determined by the method. Since the total fit deviation will depend on the fit parameter values in a very nonlinear and in most cases unpredictable way, there may be many local minima in addition to the wanted global minimum of the fit deviation. Although there are minimization algorithms which may escape from local minima, they are usually very slow and their application is not recommended for spectrum fitting.
It is more efficient in most cases to reduce the parameter ranges before the actual minimization work starts. This can be done interactively or by appropriate automatic test computations. A common problem, for example, is to find the right interference fringe order in the simulated spectrum. This can be solved quite often by scanning the thickness value on a fixed set of values in a pre-defined search range ('grid fit'). Taking the best thickness value of this test series as starting value for the thickness turned out to be sufficient in many cases.

4 The key to success: Optical constant models

4.1 Overview

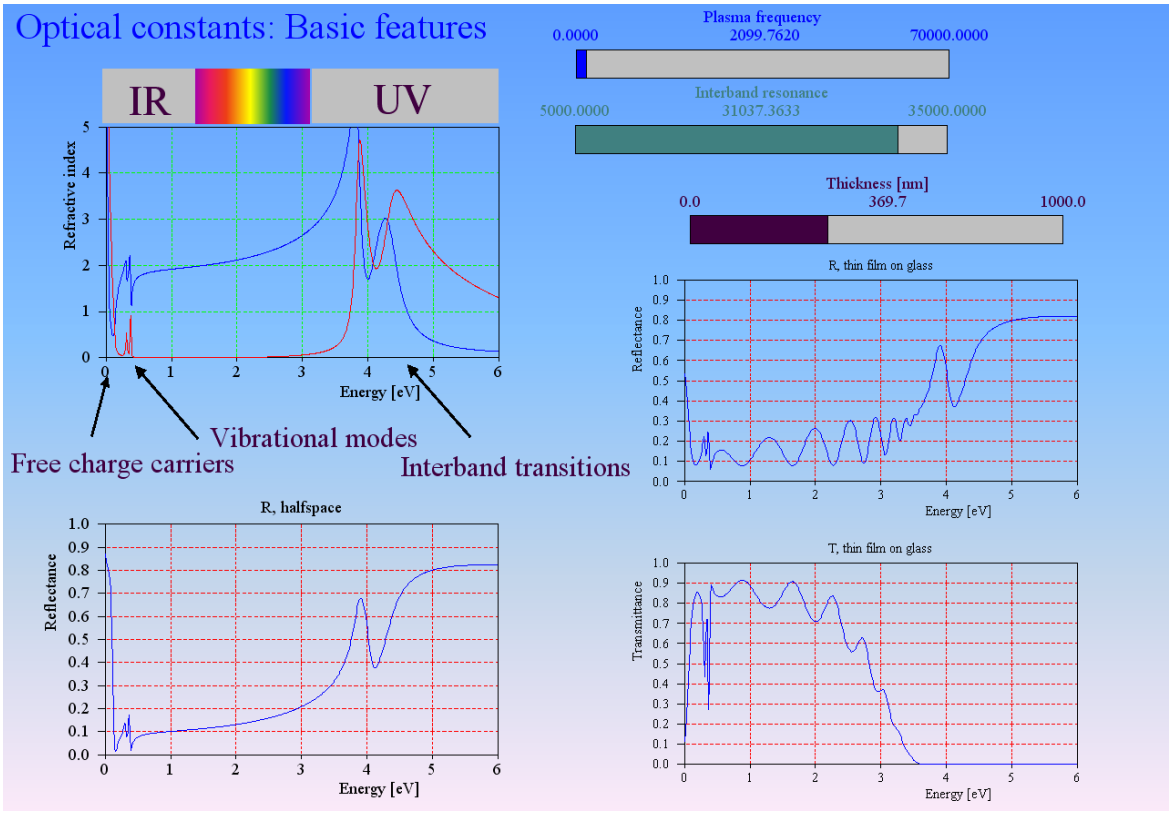
The most important step in spectrum simulation is the choice of the optical constants. If the materials in the system under investigation cannot be described with fixed literature data, flexible models have to be used. Three basic types of excitations are possible in most materials:

- Acceleration of free charge carriers by the electric field of the light wave, usually described by the

Drude model or its extensions

- Excitation of vibrational modes, i.e. oscillations of charged parts of molecules or crystal lattices. Vibrational modes are taken into account using oscillator models.
- Optical interband transitions of the electronic system. These phenomena can be described by oscillator terms, Tauc-Lorentz models in the case of crystalline materials or OJL models in the case of amorphous systems.

Quite often there is a large gap between the vibrational modes in the infrared and interband transitions in the UV. In this case the material is more or less transparent in the visible, with a small imaginary part of the refractive index, and an increase of the real part from the red to the blue (normal dispersion). In the range 1 ... 3 eV in the example below the optical constants could be approximated by the phenomenological Cauchy formula. However, if possible, the application of a physical model is preferred.

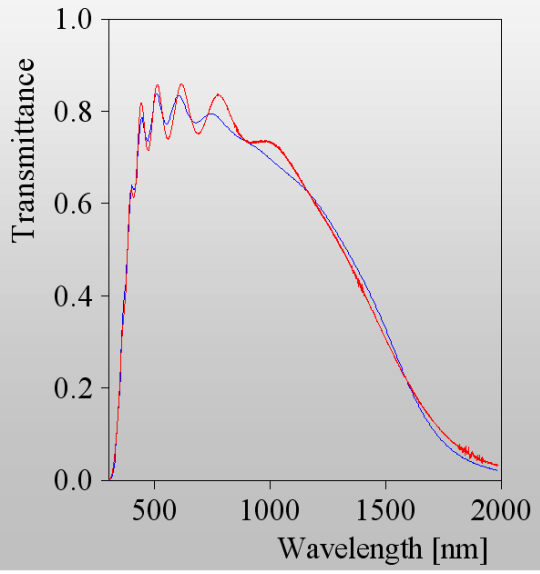


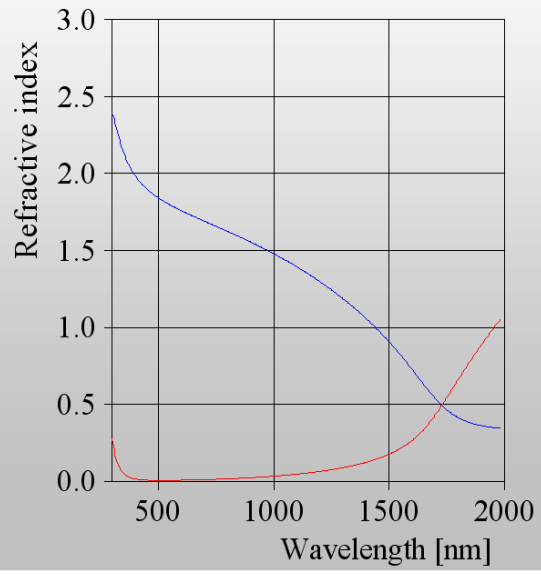
4.2 Drude model

The classical Drude model of free charge carriers leads to a simple expression of the susceptibility with only two parameters, the plasma frequency and the damping constant. If the effective mass is known, these quantities can be directly related to the charge carrier density and their mobility, or the resistivity of the material. In most cases of doped semiconductors or metals the Drude model works quite well.
However, sometimes the simple Drude model is not appropriate as shown below for the case of an ITO layer on glass.The fit in the whole spectral range suffers from the assumption of a constant damping of the electrons, independent of frequency. In this case the electron mobility is limited by scattering at ionized impurities (the doping atoms), an effect which leads to a certain frequency dependence of the damping constant.

ITO on glass: const. + OJL interband transition + Drude model

$$\chi_{Drude}(\omega) = -\frac{\Omega_{Dr}^2}{\omega^2 + \Gamma_{Dr}^2} + i\frac{\Gamma_{Dr}}{\omega}\frac{\Omega_{Dr}^2}{\omega^2 + \Gamma_{Dr}^2}$$



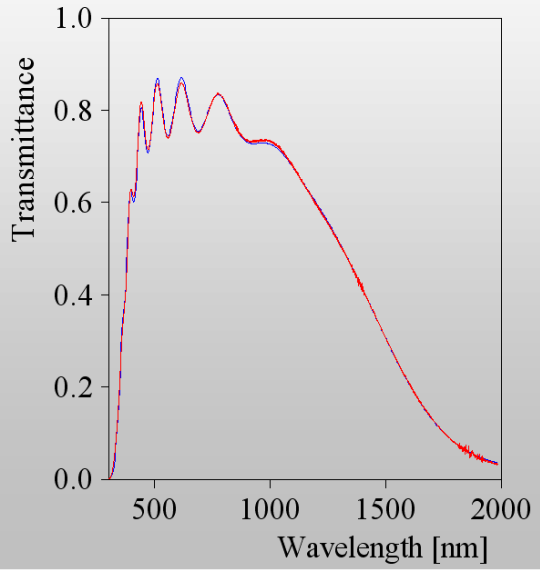


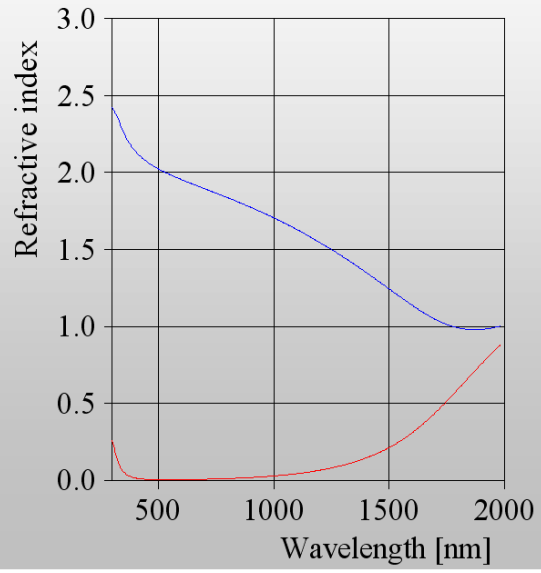
An extended Drude model with a (still quite simple) frequency dependent damping constant leads to a significant improvement of the fit with much more reliable results for the film thickness and the other model parameters such as gap energy and resistivity:

ITO on glass: const. + OJL interband transition + extended Drude model

$$\chi_{Drude}(\omega) = -\frac{\Omega_{Dr}^2}{\omega^2 + \Gamma_{Dr}^2} + i\frac{\Gamma_{Dr}}{\omega}\frac{\Omega_{Dr}^2}{\omega^2 + \Gamma_{Dr}^2}$$

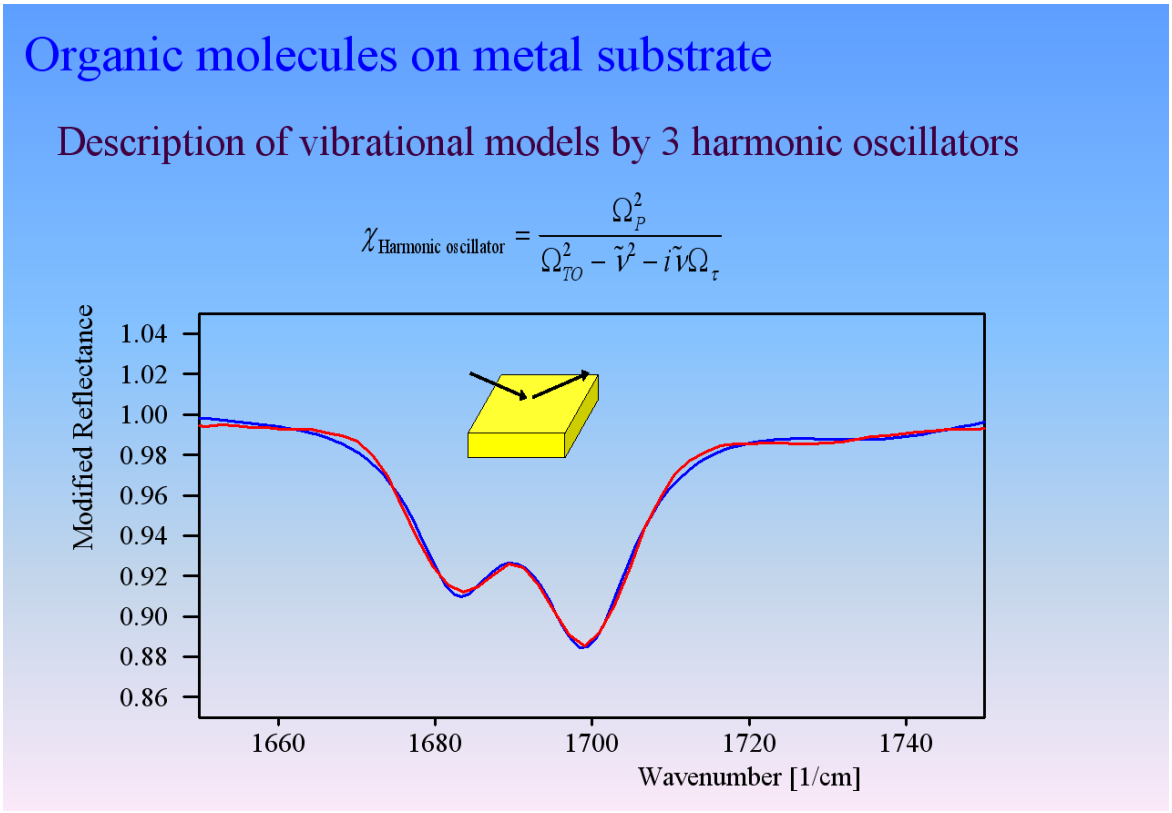
$$\Gamma_{Dr}(\omega) = \Gamma_L - \frac{\Gamma_L - \Gamma_H}{\pi}\left[\arctan\left(\frac{\omega - \Omega_{\Gamma,Dr}}{\Gamma_W}\right) + \frac{\pi}{2}\right]$$



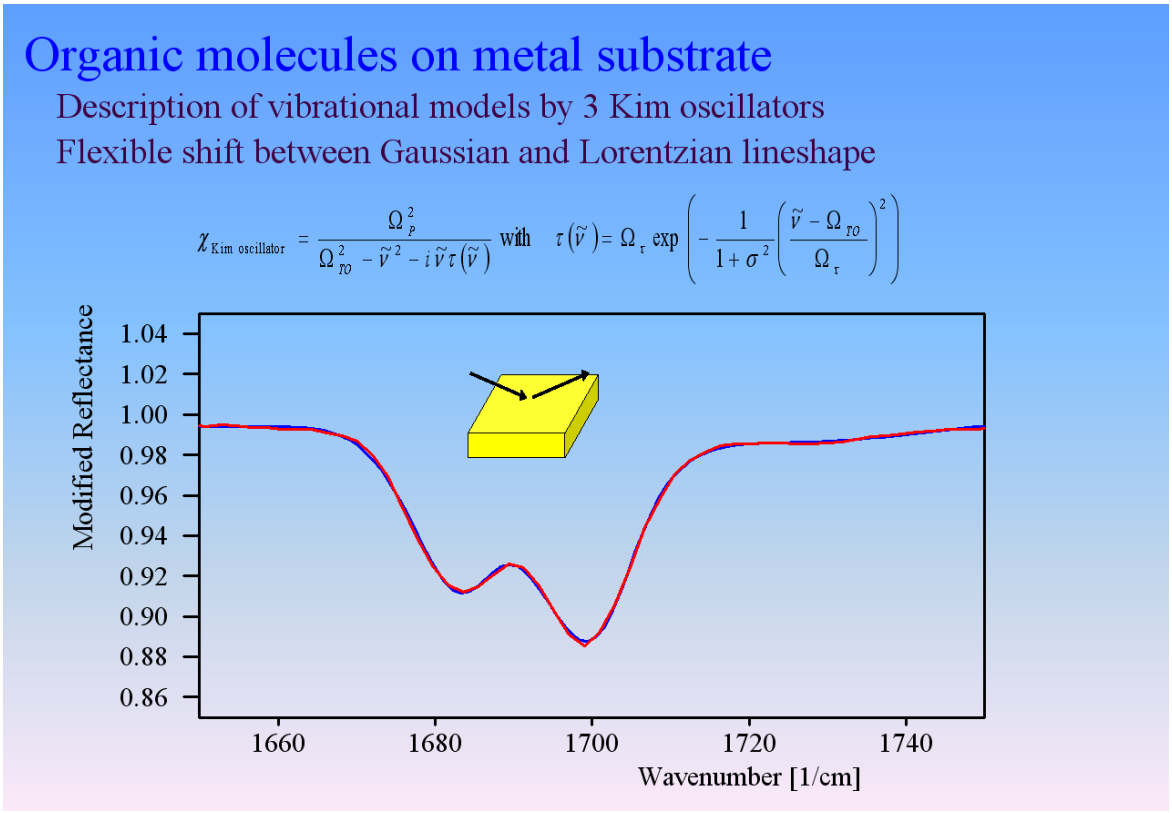


4.3 Oscillator models

Vibrational modes (with resonance frequencies that depend on the masses of the atomic cores and the strength of the restoring forces) leave 'finger prints' of a material in the infrared. These are used in numerous applications for material identification in the chemical industry.
A rough description can be achieved by summing up harmonic oscillator terms with three parameters: The resonance frequency, the damping constant (which determines the halfwidth of the corresponding absorption band) and the so-called oscillator strength (which is proportional to the concentration of the microscopic oscillators).

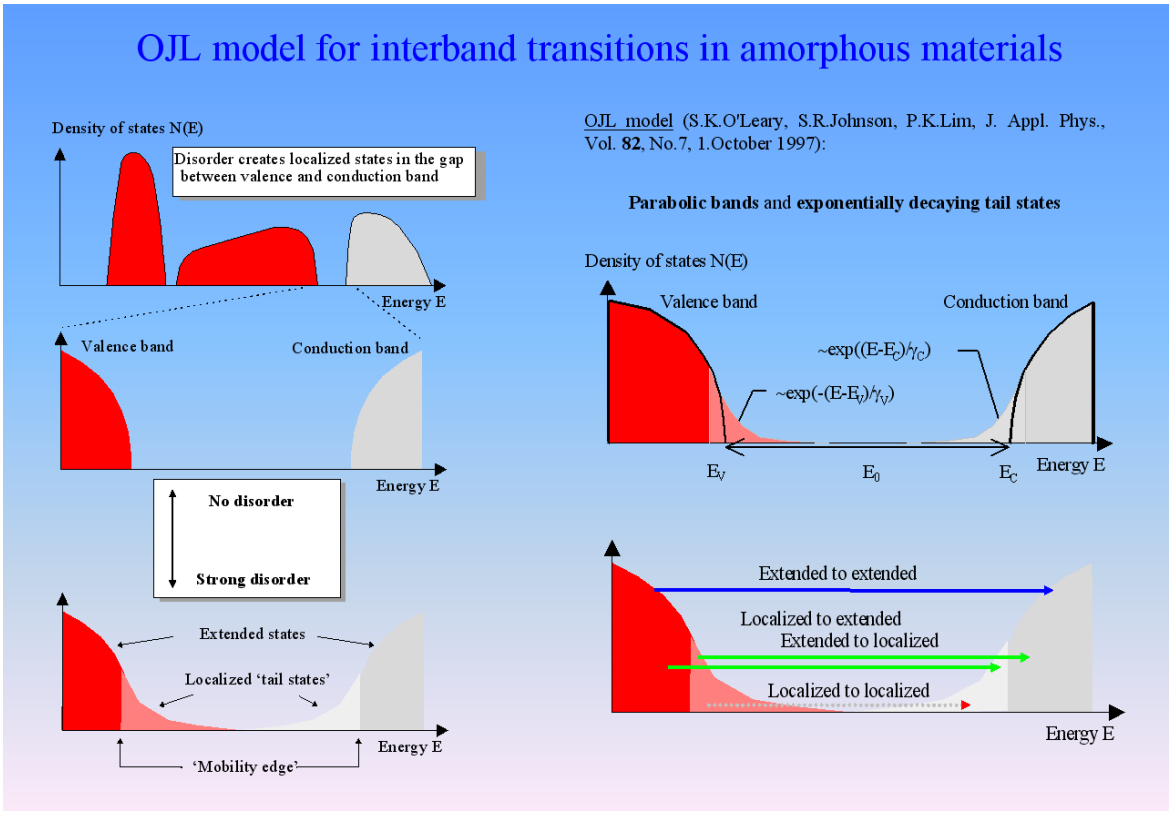


Extensions of the harmonic oscillator model are required if the line shape is not a Lorentzian. With a fourth oscillator parameter, the so-called Kim model (shown below) can describe both Gaussian and Lorentzian line shapes of absorption bands, and any lineshape in between these two extremes.

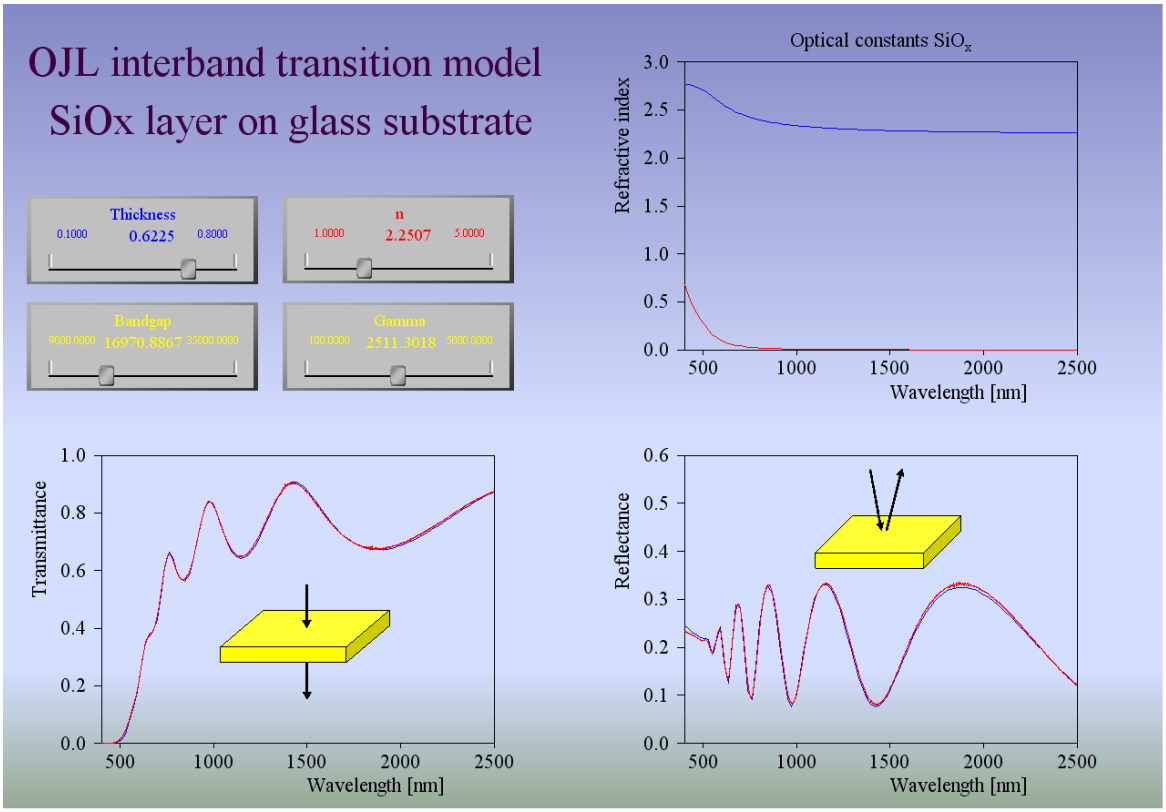


4.4 Interband transition models

Interband transition models are not easy to model. They are usually quite asymmetric, very strong and in most cases several transitions overlap each other. Often it is not even easy to see how many excitations one should use.
In addition, theoretical quantum mechanical considerations result in expressions for the imaginary part of the dielectric function only. The corresponding real part must be constructed making use of the Kramers-Kroning relation. Fortunately, the required Hilbert transform can be performed in two steps with Fast Fourier Transform algorithms which makes the computations reasonably fast on modern computers.
The so-called OJL model shown below has turned out to be very successful for amorphous oxides and nitrides. The list of materials that can be described with this still rather simple model contains SiOx, GeOx, BiOx, TiOx, SnOx, ZnOx, ...



The example below shows the fit of a reflectance and transmittance spectrum of a SiOx layer on glass, making use of the OJL model:

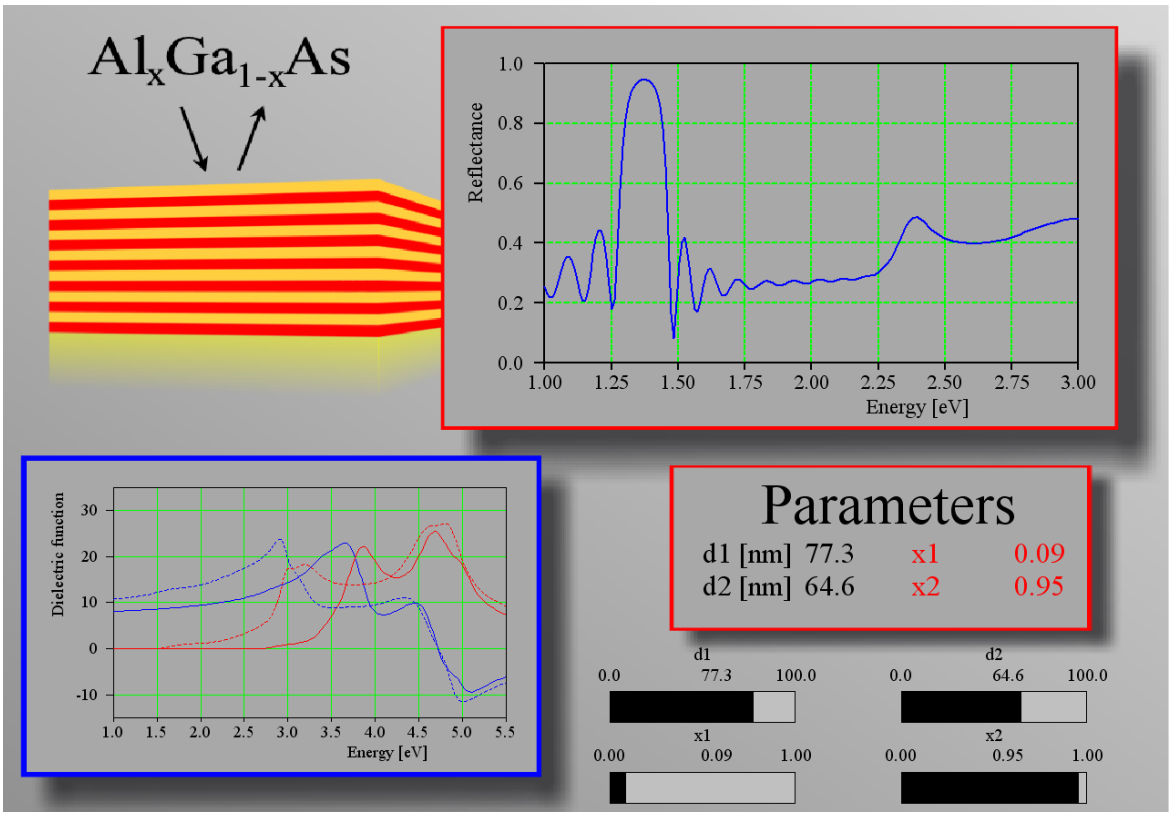


Crystalline materials can be described quite well by a sum of several Tauc-Lorentz models for

interband transitions. An example will be shown in the next section.

4.5 Varying composition: Master models

Materials with varying composition like non-stochiometric oxides or ternary or quaternary compound semiconductors have - of course - optical constants that change with composition. The example below shows the case of AlGaAs with varying Al content.
A model based on 8 Tauc-Lorentz interband transition terms has been fitted to literature data available for several Al content (x) values. 33 parameters like gap energies and damping contants have been determined for each individual value of x. Then the development of each parameter with x has been described by suitable polynomial expressions such that a smooth variation of the optical constant model with Al content x is achieved. This so-called master model is used to describe the optical properties of a AlGaAs superlattice with alternating layers of high and low Al content.



4.6 Composite materials: Effective dielectric functions

Composite materials like clusters embedded in a host, foams, porous materials or suspensions can be described by so-called effective dielectric functions if the dimensions of the microscopic inhomogeneities are much smaller than the wavelength of light. They behave like homogeneous materials with optical constants which are an average of those of the constituents. So-called effective medium theories gives mixing rules and formulas. Unfortunately, there is not a single unique mixing method but several concepts are possible. A discussion of this topic and recommendations for the right choice of effective medium theories are outside the scope of this document.

5 Examples

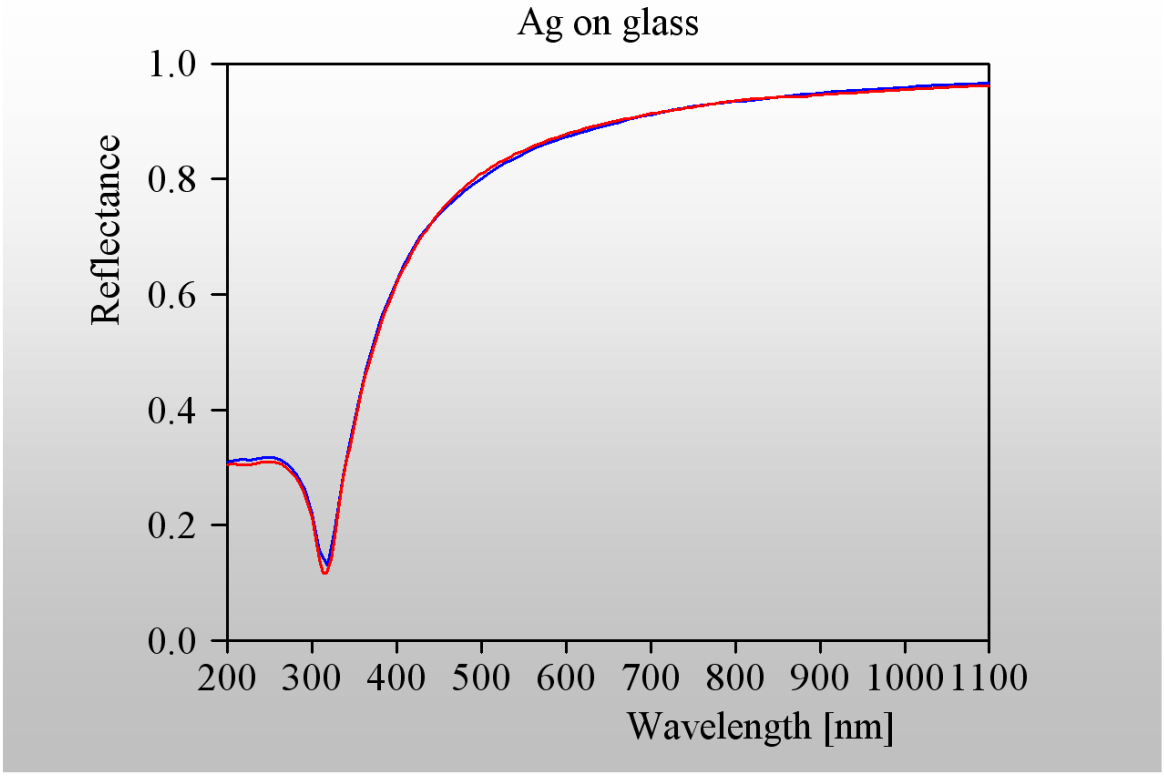
5.1 Overview

Finally some simple and advanced spectrum simulation applications are presented, in addition to the ones already shown above. The examples are

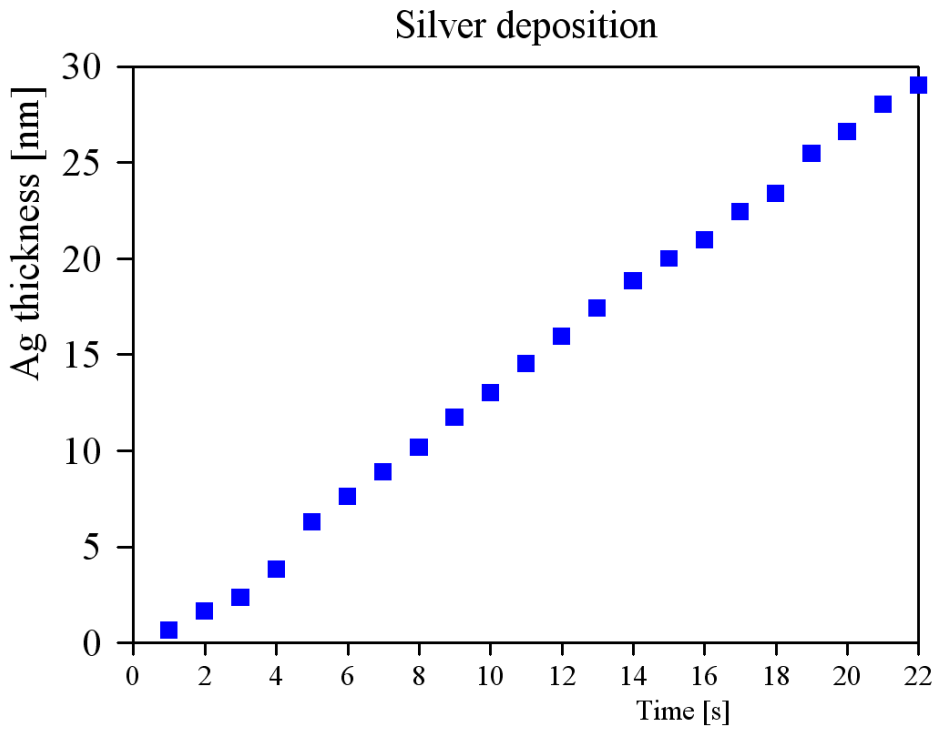
- Automated analysis of reflectance spectra of Ag layers on glass
- Analysis of an unknown new semiconductor with ellipsometry
- Simultaneous R and T analysis of CdS layers
- Determination of molecular orientation by analysis of several infrared spectra
- Porosity profile determination by simultaneous simulation of 8 reflectance spectra
- Combined reflectance and ellipsometry analysis of thin films

5.2 Batch fit example

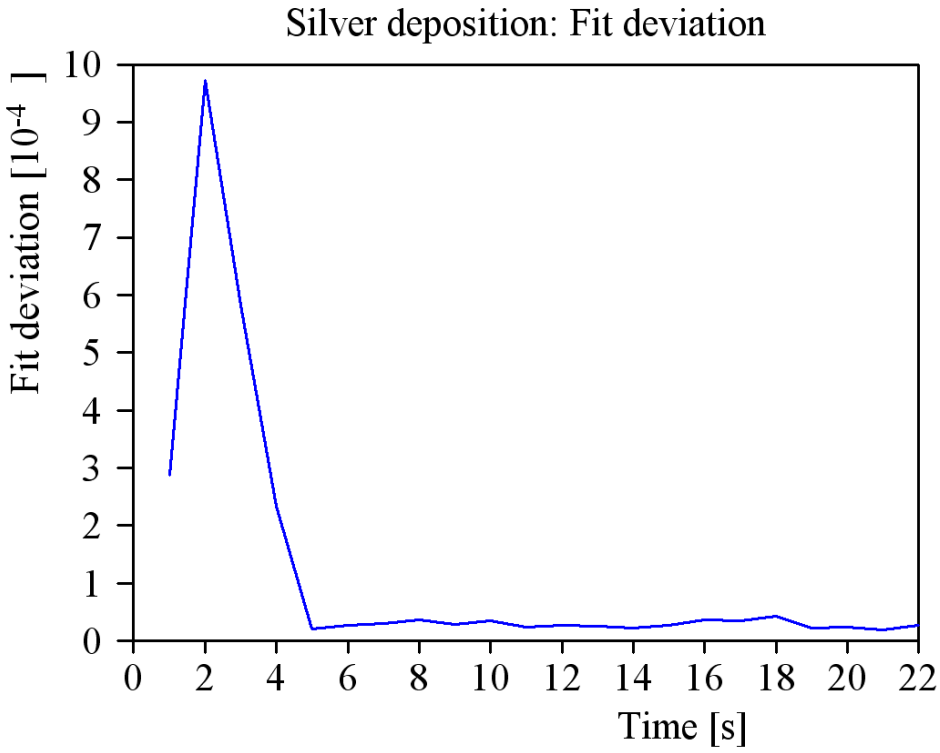
Once a working model for an analytical problem has been developed, spectrum simulation can be automized in order to process large series of spectra. Here a simple example is presented the goal of which was to determine the sputtering rate of a Ag deposition device.
A sequence of samples have been prepared with sputtering times between 1 and 23 seconds. The reflectance spectra have been analyzed with a simple model of Ag on glass (based on literature data for the optical constants). Since only the Ag layer thickness is unknown the fits are done very quickly.



The next graph shows the obtained thickness values vs. sputtering time. From the slope a sputtering rate of 1.3 nm/s can be deduced.

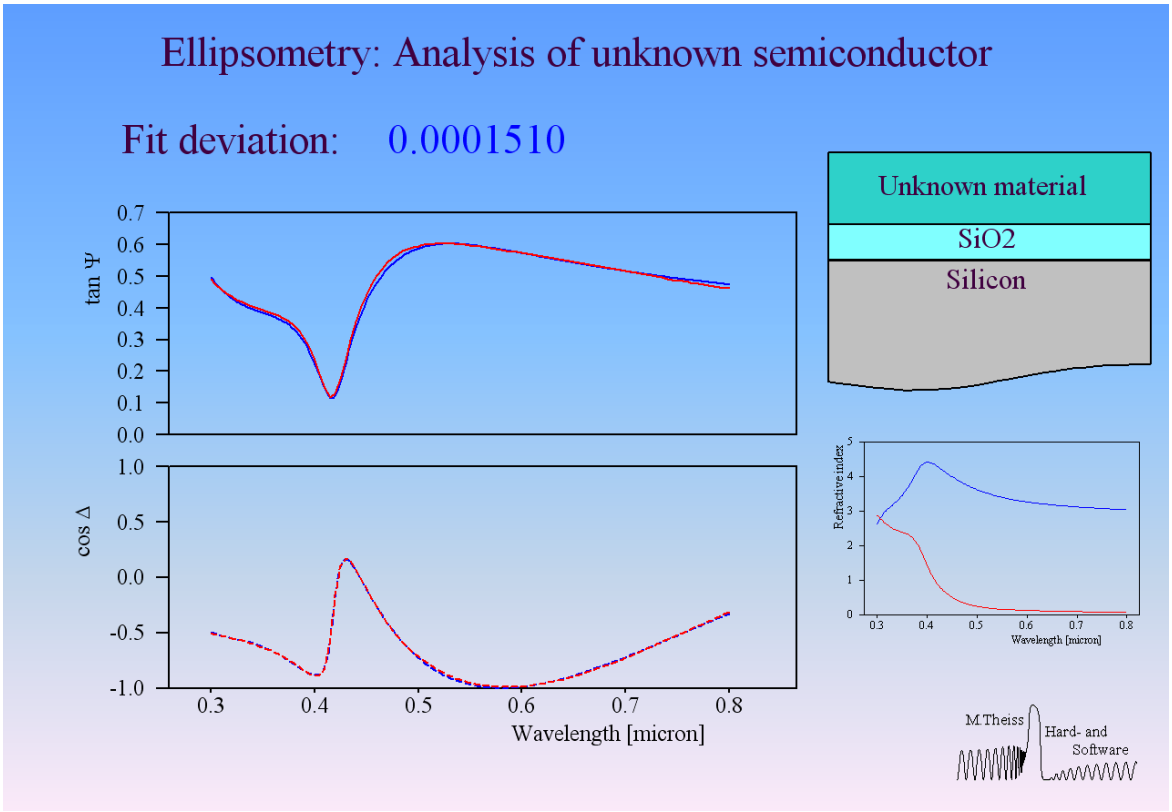


The plot of the fit deviation shows that the fit is bad for layers below 8 nm thickness. Here the model does not work well. The reason is the island growth of Ag on glass: Below a certain thickness threshold there is no continuous Ag film, but rather an island structure. In these cases an effective medium approach describing an Ag/air mixture is more appropriate.

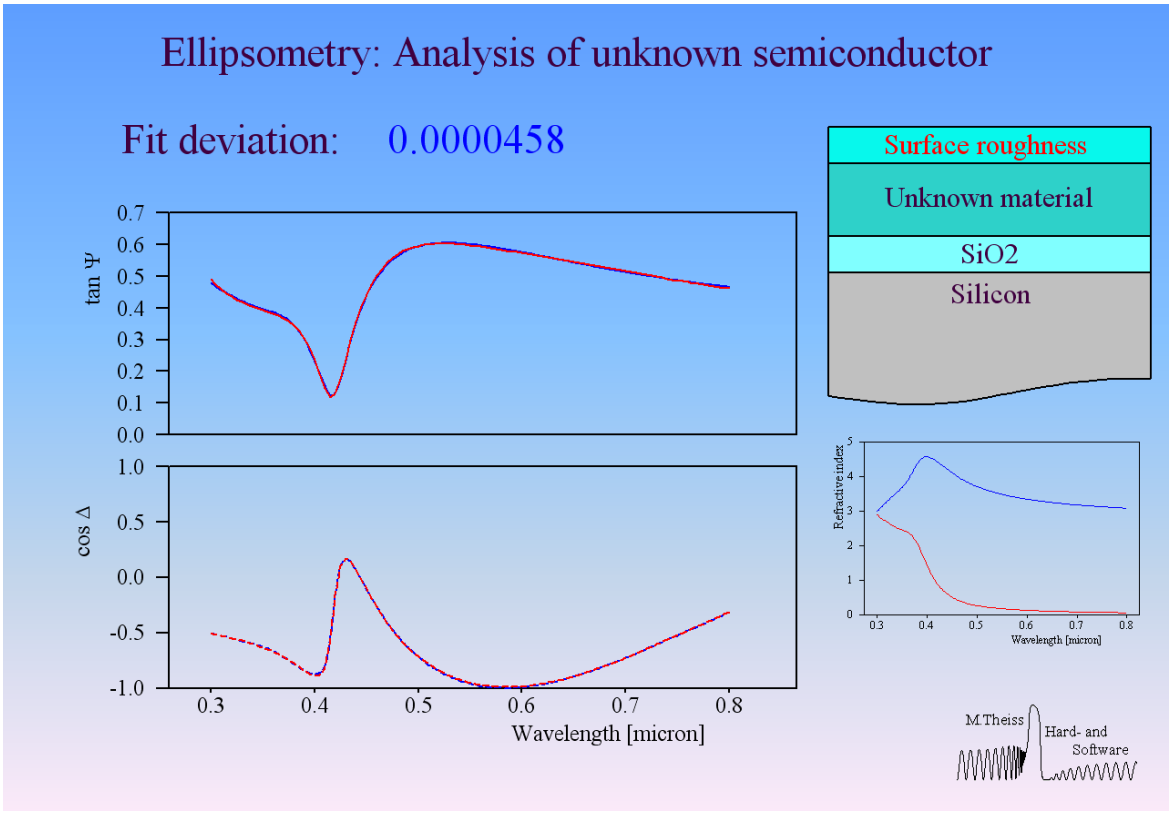


5.3 Ellipsometrie: Investigate unknown semiconductor

This example demonstrates the determination of the optical constants of an unknown semiconductor on a SiO2/Si substrate by ellipsometry. Using several Tauc-Lorentz terms the following reasonable fit was achieved:

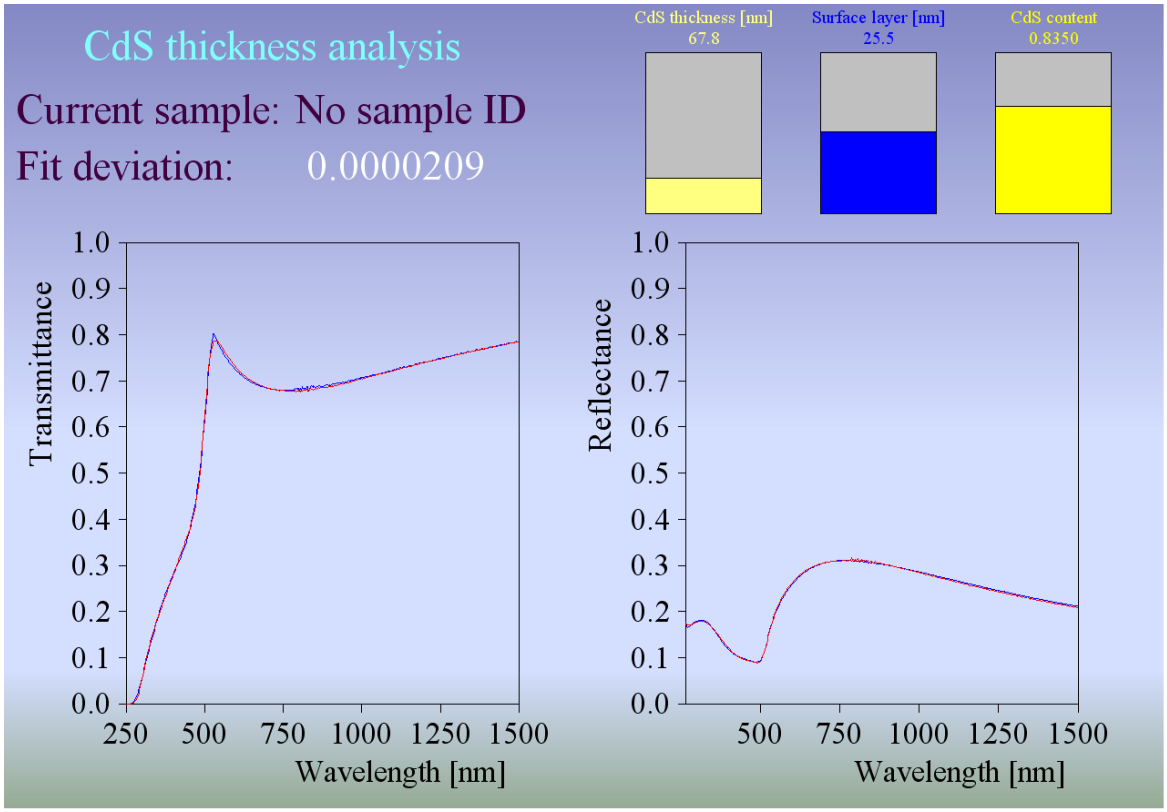


The fit can be improved introducing a thin surface layer which represents surface roughness. The layer is an effective medium mixture of the unknown material and air. The obtained optical constants differ not very much, but significantly from the ones obtained without surface roughness. In important cases the assumption of the existance of a surface roughness should be confirmed by an independent method such as AFM.

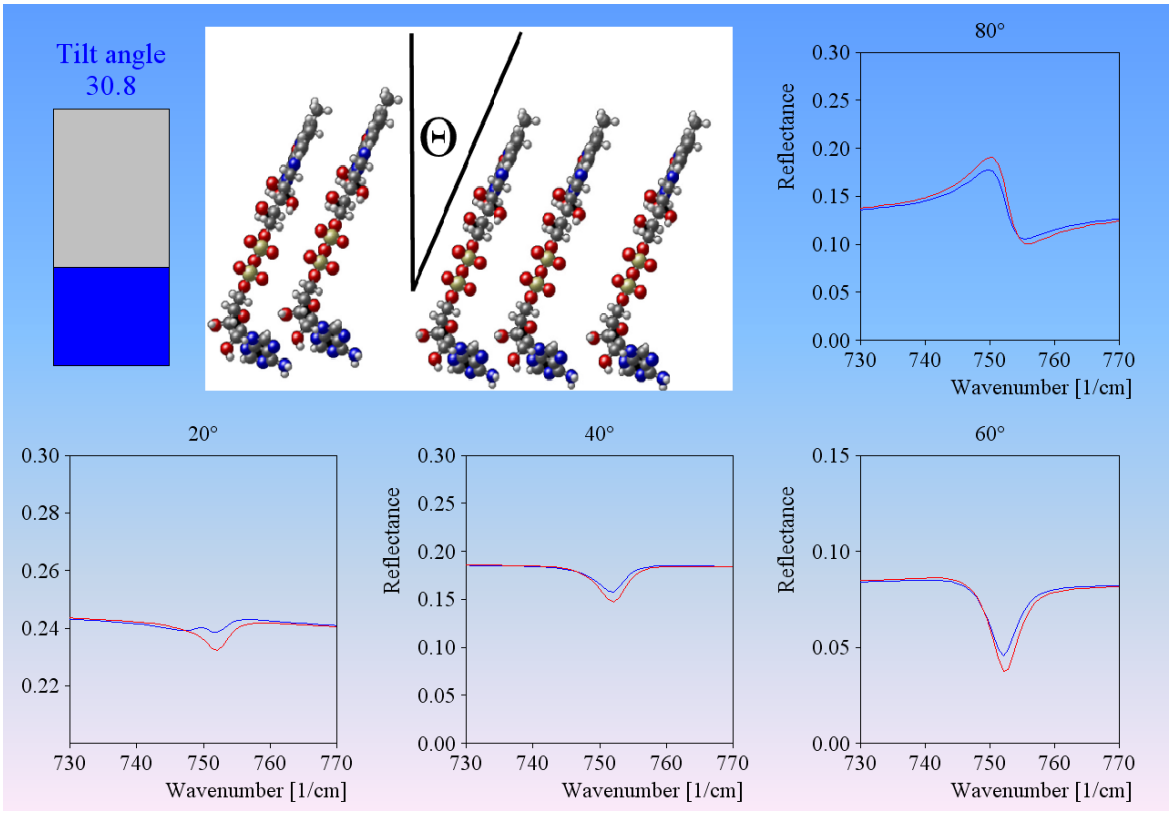


5.4 Analyzing several spectra simultaneously

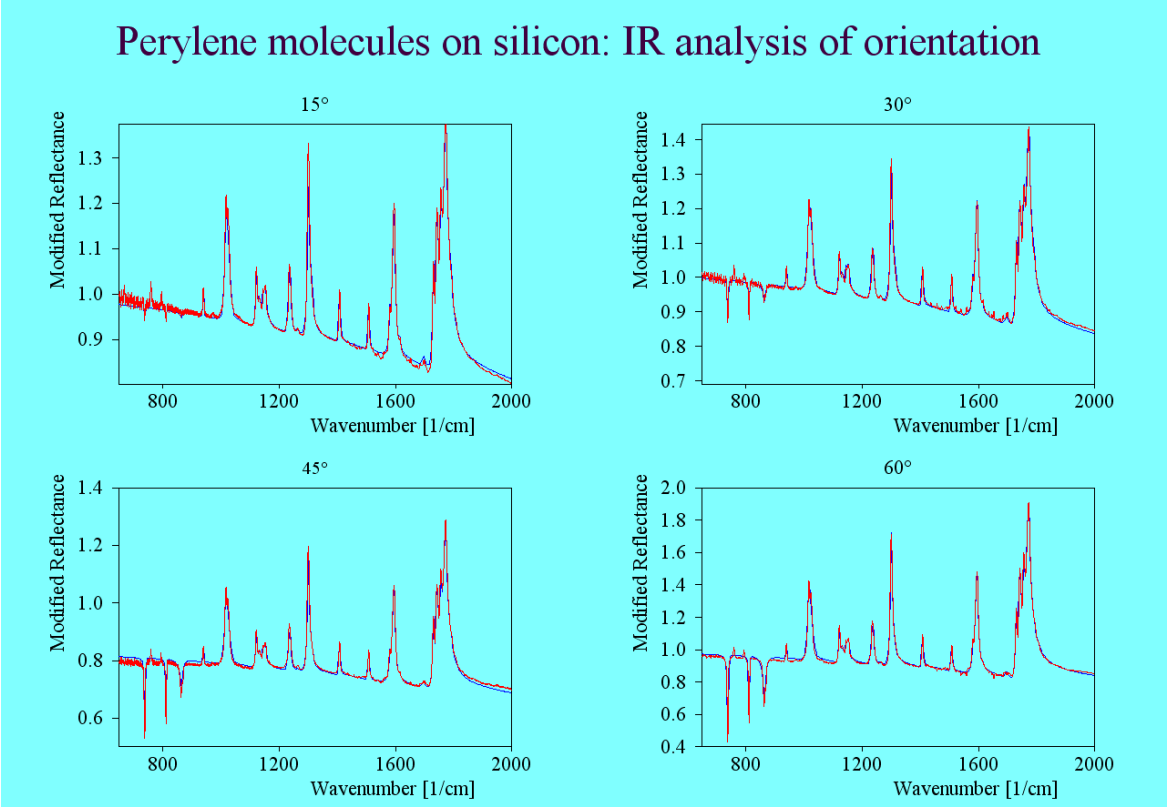
In order to increase the reliability of the obtained parameters, one can analyze more than one spectrum which may result in much more significant spectral information. In the following several 'multiple spectra' cases are shown.
In the case of transparent substrates such as glass plates one can measure R and T and analyze both spectra. In the example below the thickness of a CdS layer (with surface roughness) is determined.



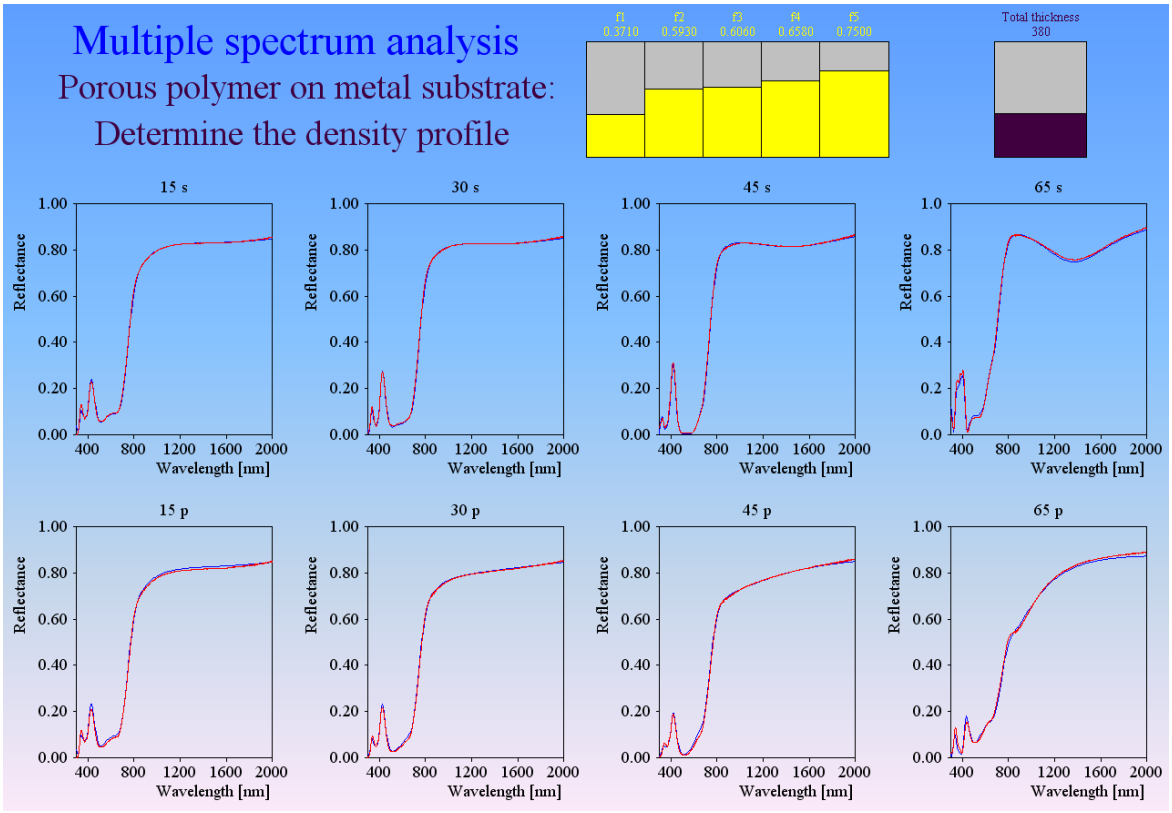
Changing the angle of incidence of the illuminating light wave one can change the direction of the electric field in the sample. The next example shows - as an artificial demo with one model oscillator - how the reflectivity of a layer of ordered molecules on a substrate changes with angle. Fitting the spectra recorded at several angles of incidence one can determine the orientation angle of the molecules.



Here is a real case of molelcular orientation analysis: For a layer of perylene molecules on a Si wafer the reflectance spectra taken at several angles of incidence are fitted simultaneously. For each vibrational mode the orientation angle with respect to the surface normal of the Si wafer could be determined. From the angular information the absolute orientation of the molecules was finally deduced.



The next example shows the analysis of 8 reflectance spectra (taking at different angles of incidence and polarization) of a porous polymer on a metal substrate. The porous layer was sampled in 5 sublayers. For each sublayer the volume fraction of the polymer (f1, ..., f5) was fitted independently, in addition to the total layer thickness. The 8 spectra contain enough spectral information for a unique determination of the density profile.



Finally an example of a combined reflectance and ellipsometry investigation is given. The optical constants of a nitride layer as well as the thickness were to be determined. An OJL model was used to model the optical constants. Both ellipsometry and reflectance could only be fitted in high quality working with two layer stacks with slightly different nitride thickness. The reason for this is that the measurements have not been performed on exactly the same sample position.