REFLECTANCE SPECTROMETRY OF TiO_2 OPTICAL COATINGS ON c-Si: THE REAL DATA BASED SIMULATION*

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The measurement of the optical parameters of thin films deposited on absorbing substrate with dispersion is presented. Reflectance was measured for normally incident light using a commercial fiber-optics spectrometer. Suggested experimental configuration is sufficiently flexible and enables the investigation of planar samples with specular surface. The same set-up can be utilized for in-situ measurements. The obtained parameters of samples were statistically tested using resampling of the measured data set. The bootstrap method, which enables to estimate the confidence intervals for calculated parameters of layers, was used. The analysis of TiO_2 films deposited on c-Si substrate is presented as an example.

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1 Introduction

The spectroscopic analysis of optical functions is a handy and reliable diagnostic method. The measured signal depends on electronic structure of bulk material, but mostly it is practically insensitive to effects localized at interfaces. The optical response of the sample can be expressed in terms of complex refractive index, which is defined as $\hat{n}(\lambda) = n(\lambda) - i\kappa(\lambda)$, where n is the real refractive index and κ is the extinction coefficient. All these parameters are the functions of the wavelength of the incident radiation.

The knowledge of the dispersion characteristics of deposited layers can yield information about both status and processes in investigated material. If the substrate is opaque, only reflectance data are available. The complex refractive index of deposited film, substrate and thickness of the film are usually unknown parameters. An effective algorithm based on unique approximate analytical solution for determination of the optical constants of a substrate covered by

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thin film was presented by Russev *et al.* [1]. The ellipsometry is often used as a powerful tool for detailed analysis of similar topics. Cormier and Boudreau in [2] introduced genetic algorithm based on random organized search to find the best solution for the inversion of ellipsometric data of thin films on semiinfinite substrate. Franta *et al.* presented in [3] complete optical analysis of hydrogenated amorphous silicon layers deposited on silicon single wafers. The influences of roughness and native oxide layer were respected in the analysis.

The reflectance spectroscopy can be utilized for thin film investigation, because it was shown, that the spectra could be analyzed for the unknown phase by dispersion methods. In consequence, the spectroscopy is capable to give the full information about the complex refractive index (see e.g. [4]). The method of reflectance spectroscopy has become widely used for determining of optical constants of strongly absorbing materials or materials deposited on such substrates. They are sometimes combined with ellipsometry to enhance their capability. Ebert *et al.* in [5] introduced original diagnostic equipment implementing non-destructive in situ controlling deposition process based on the combination of spectroscopic ellipsometry and reflectance-difference spectrometry, which enables the investigation of anisotropic films. Polit *et al.* in [6] published the study of bulk phonons in thin films, utilising the infrared reflection-absorption spectroscopy. Surdutovich *et al.* ([7]) developed a simple reflectometric method, using the shadow Brewster angle (SBA) for easier separation of the refractive index and thickness of a transparent film. The method can be used for weakly absorbing films deposited on a substrate with an arbitrary absorption.

Optical reflection spectra, at normal incidence, were analyzed in different spectral regions. The optical constants of the thin film and substrate and the thickness of the film can be accurately determined using the method based on maxima and minima of the reflected spectrum (see Swanepoel [8]). Gonzáles *et al.* in [9] discussed the dispersion of refractive index in terms of the energetical models of the material. Müllerová and Mudroň in [10] performed the detailed theoretical analysis of reflectance spectra and compared the results with experiment.

Attempts were made to perform the calculation to fit the reflectance data directly (in [9]). Nenkov and Pencheva in [11] tested the transmittance spectra with theoretical dispersion equation of the finite-power-series type in order to find the best fit of the parameters of thin TiO_2 film. The best-fit results for complex refractive index were found to be in agreement with theoretical dispersion relation.

The values of structure parameters are calculated numerically. The obtained results can be dependent on quality of approximation of starting values of parameters, because the optimization task is often badly conditioned. One possible solution of this problem was presented in [2]. Tabet and McGahan in [12] combined the artificial neural network to find good initial estimates for thickness and dispersion model parameters from spectroscopic reflectometry data. These are used as the starting point for the Levenberg-Marquardt algorithm.

The inversion of reflectance data is a procedure, which may give non-unique results. In order to remove their ambiguity, different techniques are used. We mentioned in preceding paragraphs a small number of them. The aim of this paper is to present a new method of verification of inverted data in reflectance spectrometry based on the non-parametrical statistical test.

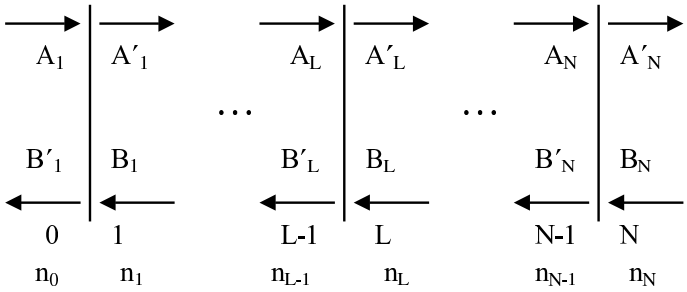

Fig. 1. Schematic diagram of light transmission through set of isotropic homogeneous films.

2 Reflectance of layered structure

Most thin film systems can be represented as a structure composed of parallel-sided lamellae, which are in close contact. The application of Maxwell equations to such system leads to differential equations, which can be solved analytically only in some special cases. The abrupt interface with specular surface can serve as an example. Fortunately, most of interfaces are of this type and the deposited films can be often considered as the "nearly homogeneous" layers on homogeneous substrate. Generally, the solution must be found numerically.

Matrix formalism is often used for description of such layered systems. The principle is well known; more detailed description can be found e.g. in book of Azzam and Bashara [13] for the set of homogeneous layers. The usage of this formalism for more general case presented Ohlídal and Franta in [14]. If we consider that the light passes through a system of homogeneous layers, each of which is characterized by refractive index $\hat{n}_i$ and thickness h_i, where i is the index of the layer as depicted in Fig. 1, the complex amplitudes of the reflected and/or transmitted waves can be described by the matrix equation:

$$\begin{pmatrix} A_i \\ B'_i \end{pmatrix} = \frac{1}{t_{i,i+1}} \begin{pmatrix} 1 & r_{i,i+1} \\ r_{i,i+1} & 1 \end{pmatrix} \begin{pmatrix} A'_{i+1} \\ B_{i+1} \end{pmatrix} = R_{i,i+1} \begin{pmatrix} A'_{i+1} \\ B_{i+1} \end{pmatrix} \tag{1}$$

Here A_i, B_i, A'_i, B'_i are the corresponding amplitudes, their meaning is clarified in Fig. 1. They are the vectors, because they correspond to the s^- and p^- waves. Quantities $r_{i,i+1}$ and $t_{i,i+1}$ are the Fressnel reflection and transmission coefficients given by equations $r_{i,i+1} = (\hat{n}_i - \hat{n}_{i+1})/(\hat{n}_i + \hat{n}_{i+1})$, $t_{i,i+1} = 2\hat{n}_i/(\hat{n}_i + \hat{n}_{i+1})$ in the case of normal light incidence.

Similarly, the phase variation of the (normally incident) wave is expressed as:

$$\begin{pmatrix} A'_i \\ B_i \end{pmatrix} = \frac{1}{t_{i,i+1}} \begin{pmatrix} \exp[i\frac{2\pi h_i n_i}{\lambda}] & 1 \\ 1 & \exp[-i\frac{2\pi h_i n_i}{\lambda}] \end{pmatrix} \begin{pmatrix} A_{i+1} \\ B'_{i+1} \end{pmatrix} = S_i \begin{pmatrix} A_{i+1} \\ B'_{i+1} \end{pmatrix} \tag{2}$$

Therefore, the relation between the amplitudes of incident and reflected light, which are denoted as A_0 and B'_0 is

$$r = \frac{B'_0}{A_0} = \frac{M_{2,1}}{M_{1,1}} \tag{3}$$

and the reflectance is

$$R = \mid r \mid^2. \tag{4}$$

Term

$$M = R_{0,1}S_1R_{1,2}\cdots R_{n-2,n-1}S_{n-1}R_{n-1,n} \tag{5}$$

is called the overall transfer matrix.

The last expression is a universal one, because it holds for arbitrary number of layers. However, the effectivity of the numerical computation can be significantly improved by rewriting the equation for given case, e.g. for a single film deposited on homogeneous substrate.

On the other side, any preliminary information can have an improving effect. The number of layers plays the role of such information. The second example is the application of the envelope method, because the knowledge of the position of interference maxima and minima is another kind of additional information, which facilitates the separation of calculated layer parameters.

As the first step, the experimental determination of layered structure involves the measurement of the dispersion of reflectance (or transmittance). The second step is the search for such set of parameters, which minimizes the difference between the experimental and calculated reflectance.

We express the complex refractive index in the form

$$\hat{n}_l(k) = \sum_{i=0}^{M} \hat{n}_{l,i} \cdot T_i(a + b \cdot k) \tag{6}$$

where l is the order of layer and k is the wavenumber. Symbol $T_i(x)$ denotes the Legendre polynomials. The orthogonal polynomial base was used only for our convenience and in other aspects it brings only negligible effect. Numbers a and b transform the interval $k = \langle k_{min}, k_{max}\rangle$ to the interval $\langle -1, 1\rangle$. Term M is the order of the approximation. Value of $M < 2$ was used in our calculations.

3 Inversion of experimental data and bootstrap

We used the mean square deviation between predicted and measured data as the objective function. This function is non-linear in regard to the calculated parameters and it minimization must be performed numerically. Standard simplex method based on Nelder-Mead algorithm was used for this purpose. The more detailed numerical simulations confirmed that the objective function usually contains more local minima. Their positions and values are rather sensitive to small perturbations of input data. In other words, the calculated results are extremely sensitive to the measurement errors. Practically, the minimization is an inverse task, which can be badly conditioned by its nature. The existence of minimum doesn't guarantee that the corresponding result is the true value; therefore, some additional verification is necessary. Some authors use algorithms that enable to classify the solutions in order to select the optimal value ([2], [12]). We decided to use the statistical test based on confidence intervals. Because the error distribution function is unknown, the non-parametric test should be used. The resampling procedure, so called bootstrap, seems to be suitable for this purpose.

We introduced this test as a tool for proofing the reliability of computed structure parameters. Regarding previous remarks, a verification procedure should be the necessary part of the measurement, especially if a dispersing or absorbing structure is investigated. Tabet and McGahan [12] suggested the method based on artificial neural network and the Levenberg-Marquardt

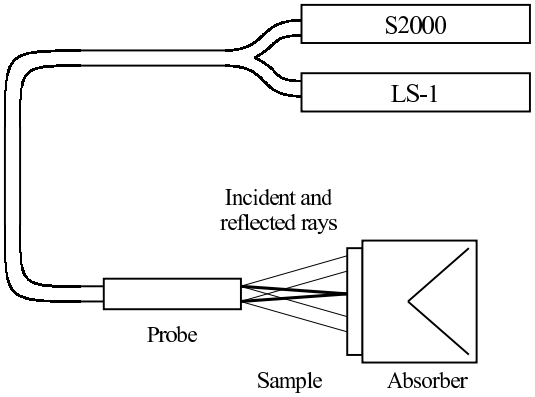

Fig. 2. Reflection-absorption spectrometric device based on fiber optics spectrophotometer S2000. The incident and reflected rays are depicted as bold lines.

algorithm, which enables to perform the necessary computations on data set containing a great uncertainty. Probably there is not any simple and reliable rule that could help to judge which input data are good or badly conditioned.

Bootstrap is a procedure based on data set resampling, which was developed by Efron [15]. It enables to judge the uncertainty of statistical estimators obtained from (usually small) samples, without prior assumptions about the underlying probability distributions. In form used in this analysis, it can be considered as a non-parametrical test, which avoids restriction and sometimes uncertain parametric assumption about the form of the underlying population. The more detailed description of this approach can be found in books [15] or [16]. The book [17] deals with variety of statistical methods based on resampling.

Bootstrap is a special kind of simulation, namely data based simulation. The simulation is made from a data-based estimate of population at it learns about the properties of a statistical procedure for the data set. The common principle is based on forming many new data sets of the same size as the measured one. These sets are created by drawing a random selection with replacement from the original observations.

4 Experimental set-up

The basic experimental scheme is depicted in Fig. 2. The set-up consists of the fiber optics spectrometer Ocean Optics 2000 supplied with light source LS-1 and a test probe. The light emitted by the launching fiber in probe is reflected from the sample surface and a part of it is collected by sensorial fiber. Such probe geometry ensures that the intensity of the parasitic background illumination is low. As it can be seen from Fig. 2, both the incident and the reflected rays are nearly parallel to the normal to surface of sample, if the distance between ends of both fibers is sufficiently small in comparison with the distance between the probe end and sample. This condition can be easily fulfilled in praxis, because the distance between fibers is approx. 100 μm, while probe is localized $\sim$ 20 mm above the surface of the sample. The parallax between illuminating and sensoric fiber is negligible. Small parallax results in small deviation of

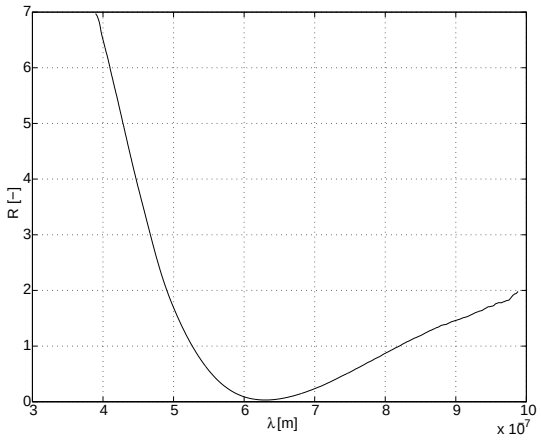

Fig. 3. Reflectance of sample A (in arbitrary units).

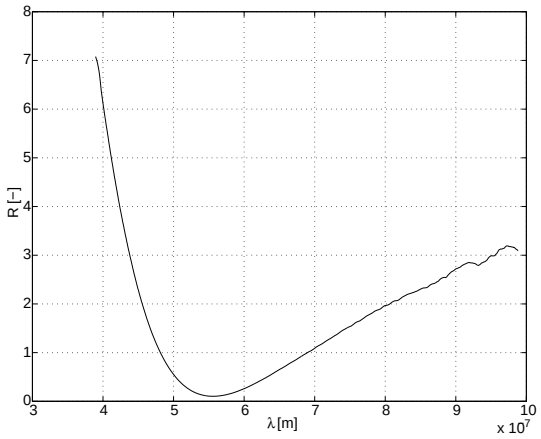

Fig. 4. Reflectance of sample B (in arbitrary units).

illuminating beam from normal, which is less then 1°. Moreover, this setting is rather insensitive to the small tilting of sample. The diameter of illuminated area on the sample surface estimated from the effective diameter of both fibers is approximately 100 μm. This enables to achieve greater spatial resolution in comparison with standard spectroscopic devices. The reflected light is collected and focused onto high sensitive linear CCD detector, which can perform precise measurements in spectral range 400-1000 nm. The device was calibrated using plate from pure silica glass, which was taken as a referential reflective element.

5 Results and discussion

The investigated samples were single crystal wafers cut at direction (100), and covered with thin TiO_2 film. The films were prepared by sol-gel technique and subsequently annealed. Sample A

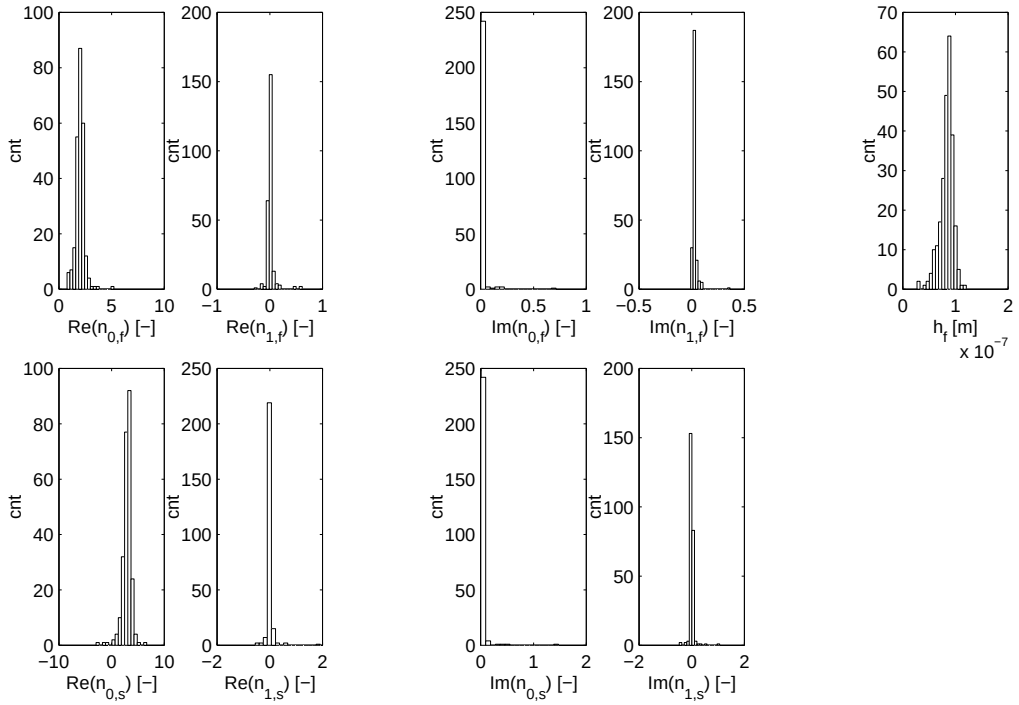

Fig. 5. Bootstrap replications of regression parameters for sample A. Real and imaginary parts of coefficients (the same as defined in Eq. (6) and thickness of the film is depicted separately. Subscript "f" relates to film parameters ($l = 2$), subscript "s" relates to substrate parameters ($l = 3$).

was treated at 300 °C, sample B at 500 °C in order to obtain the stable layer. Their reflectance spectra are depicted on Figs. 3 and 4. The goal of fitting process was to find the parameters of structure $\hat{n}_{i,j}$, h_i [see Eq. (6) and Eqs. (1)-(5)], which give the best approximation of the measured spectra in the sense of the least squares approximation. Because the thickness of TiO_2 layer is very small, only one interference minimum is observable in the entire scanned spectral range. Due to this fact, the film thickness and the refractive index cannot be found from the envelopes of interference pattern and must be derived numerically from the fit. This is the main reason, why the task is poorly conditioned. In our calculation we considered that the dispersion of TiO_2 film and Si substrate is rather small in given interval of wavelength. In accordance with this assumption, the values of all but the 0th order terms $\hat{n}_{l,i}$, $i > 0$ in polynomial approximation were searched in the neighbourhood of zero. Only 0-th and 1st orders of approximation were used in fitting procedure.

The resulting reflectance spectra combine:

a) The effects of absorption in both titanium dioxide film and silicon substrate;

b) Interference in thin film. Because the thickness of covering layer is small, the interference pattern cannot be "recognized" (only one interference minimum is observable in the entire scanned spectral range).

Algorithm searched for the parameters of such a modeling structure, the reflectance of which

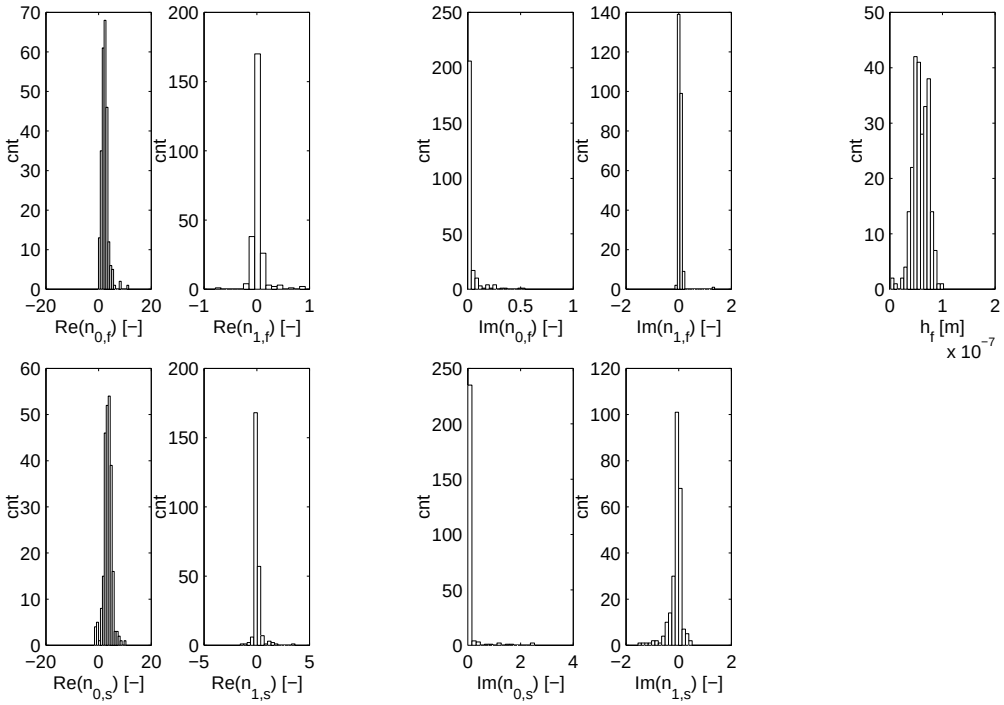

Fig. 6. Bootstrap replications of regression parameters for sample B. Real and imaginary parts of coefficients (the same as defined in Eq. (6) and thickness of the film is depicted separately. Subscript "f" relates to film parameters ($l = 2$), subscript "s" relates to substrate parameters ($l = 3$).

is as close as possible to the reflectance of the investigated sample in given wavelength range. The parameters of this modeling structure are the approximation of actual ones.

An improved version of the percentile method called BC_a ("bias-corrected and accelerated", described in [16]) was used to produce the confidence interval. Resampling of data sets was repeated 250 times for both samples A and B. Figs. 5 and 6 show the results of this procedure. Table 1 contains the values of the calculated refractive indices of both layer and substrate, as well as the thickness of the TiO_2 films. We used a usual 5% confidence limit for the confidence intervals in this table.

In spite of good agreement between predicted and calculated values, the calculated intervals show some dispersion of parameters. As it can be seen, the confidence intervals are non-symmetrical with regard to the parameters. This indicates, that standard tests, which nearly always imply the normal error distribution, can be less effective in this case, or even can give erroneous results.

The influence of temperature of annealing was investigated. The results of comparison between sample A and B show that the refractive index of TiO_2 depends slightly on the applied temperature, but their thickness is more sensitive to the treatment. The decrease of the thickness can be connected with decreasing porosity of the titanium dioxide film during annealing process. On the other hand, the relatively slow increase of refractive index is not in the relation with this.

Sample A

i	0		1	
Re($n_{f,i}$)	2.04	[1.710, 2.34]	0.05	[-0.02, +0.1]
Im($n_{f,i}$)	0.1	[0.06, 0.16]	-0.05	[-0.12, 0.12]
h_f [nm]	75	[40, 93]	-	-
Re($n_{s,i}$)	3.85	[2.00, 4.8]	0.08	[0.01, 0.11]
Im($n_{s,i}$)	0.08	[0.02, 0.12]	-0.01	[-0.11, 0.8]

Sample B

i	0		1	
Re($n_{f,i}$)	2.18	[1.45, 2.87]	0.09	[-0.04, 0.05]
Im($n_{f,i}$)	0.07	[0.05, 0.18]	0.10	[0.05, 0.15]
h_f [nm]	62	[38, 90]	-	-
Re($n_{s,i}$)	4.05	[2.85, 5.91]	-0.09	[-0.17, 0.20]
Im($n_{s,i}$)	0.16	[0.07, 0.22]	-0.10	[-0.21, 0.13]

Tab. 1. Regression parameters of TiO_2 film and substrate for samples A and B. Coefficients were defined in Eq.(6). Left value in each column is the estimated parameter, right is the confidence interval. Subscript "f" relates to film parameters ($l = 2$), subscript "s" relates to substrate parameters ($l = 3$).

We suppose that this is the result of growth of SiO_2 layer on substrate during annealing. However, we were not able to verify its existence in our computational model (adding a layer of SiO_2 between TiO_2 film and substrate), because we got statistically insignificant results for this layer. Chemical processes in the TiO_2 film, taking place during annealing between 300 °C and 500 °C, can participate in this effect too.

The attempt to estimate high order terms $n_{l,j}$, $i > 1$ was unsuccessful, because the obtained results were statistically insignificant (with regard to confidence intervals). However, in this case the fitting process resulted still in apparently good approximation, although rather unstable and sensitive to data fluctuations.

This has a more general consequence. Some of the quantities in Table 1 are charged by relatively great errors, although their estimate seems to be realistic. This is caused by badly conditioned task, mainly as a result of the small thickness of deposited film. The usage of the bootstrap test enabled us to discover this fact and to make the estimation of both the parameters and their errors too. This way, the presented modification of data based simulation can help to improve the reliability of reflectance spectroscopy method.

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