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ELLIPSOMETRY OF THIN FILMS[1]

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In this paper a brief review of ellipsometric methods is presented for analyzing thin films. Examples of using these methods will be introduced as well. By means of results obtained using the ellipsometric methods introduced their practical meaning will be illustrated. It will be shown that the ellipsometric method can be tilized for analyzing single layers and multilayer systems in a successful way.

1 Introduction

Thin film systems are often encountered in practice. Therefore methods for analyzing these systems must be available. Optical methods represent an important group of the analytical methods suitable for characterizing the thin film systems. Ellipsometric methods belong to the significant optical methods used to characterize these systems very frequently in various branches of both the fundamental and applied researches. Moreover the ellipsometric methods are often applied even in various branches of industry for checking miscellaneous devices based on the thin film systems. Ellipsometry is therefore the important physical technique whose methods are developed extensively within both the fundamental and applied researches in the last years.

In this contribution a review of the ellipsometric methods for the characterization of the thin film systems will be presented. Attention will be paid to a classification of these methods from the point of view of their practical utilization. Thus the main methods of both monochromatic and spectroscopic ellipsometries having a practical meaning will be discussed. Principles of these methods will be described briefly. All the ellipsometric methods mentioned will be illustrated by means of the characterization of chosen thin

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film systems relevant from the practical point of view. This illustration of employing the individual methods will be utilized for demonstrating a precision and reliability of these methods. Attention will be focused not only to single layers but the ellipsometric analysis of multilayer systems chosen will be presented as well.

2 Classification of the ellipsometric methods

Experimental methods of ellipsometry can be divided into two basic groups. The first group consists of the ellipsometric methods applied for experimental studies of the thin film systems after their preparation. They are usually utilized outside of the technological equipments. These methods are called ex-situ ones. The latter group is formed by the methods applied during the growth of the thin film systems. These methods are mostly employed for checking the properties of the systems originating into the corresponding technological equipments. They are called in-situ methods.

Both the ex-situ and in-situ ellipsometric methods can be classified into two groups:

- monochromatic methods
- spectroscopic methods

The monochromatic methods and spectroscopic methods can further be divided into two other groups:

- single angle of incidence methods
- multiple angle of incidence methods

Thus in practice one can encounter the following ellipsometric methods: the monochro-matic single angle of incidence methods, monochromatic multiple angle of incidence methods, spectroscopic single angle of incidence methods and spectroscopic multiple angle of incidence methods. In principle all these methods consist of two methods, i. e., non-immersion methods and immersion methods.

Within the monochromatic and/or spectroscopic methods the values of the ellipso-metric parameters of the thin film systems are measured at single wavelength and/or a family of wavelengths from a certain spectral region. Single and/or multiple angle of incidence ellipsometric methods are based on measuring these quantities at one and/or several angles of incidence on the systems. The non-immersion methods enable us to measure the ellipsometric parameters of the systems in one ambient (mostly in air) whereas the immersion ones give the possibility to measure these quantities in various ambients (e. g., in different non-absorbing liquids).

The foregoing methods outlined are employed within ellipsometry except the meth-ods of immersion spectroscopic ellipsometry (these immersion spectroscopic methods of ellipsometry are usable in principal but their application has not been realized in practice so far to our knowledge). Further, note that in practice only non-immersion and single angle of incidence methods are employed as the in-situ ones.

Below we shall present some representative methods of ellipsometry having a prac-tical meaning that were applied in our laboratory.

2.1 Monochromatic single angle of incidence method

This method can be called monochromatic single angle of incidence (MSAI) ellipsometry as well. Within this method the ellipsometric parameters Ψ (azimuth) and Δ (phase change) of the thin film systems are measured at one wavelength and one angle of incidence. Thus the values of the two independent ellipsometric parameters Ψ and Δ are measured for the system studied if this method is applied (the measurements of Ψ and Δ are usually performed in air).

We used MSAI ellipsometry, for example, for ex-situ measurements of single layers of non-absorbing anodic oxide on GaAs substrates. The values of the ellipsometric parameters were measured for the wavelength of 632.8 nm at the angle of incidence $\theta_0 = 70°$. The values of the optical constants of the GaAs-substrates were taken from the literature (see Ref. [1]). The values of the ellipsometric parameters, i. e., the values of Ψ and Δ, were treated by using an iterative numerical procedure enabling us to evaluate the values of both the optical parameters of the single layers mentioned in a reliable way. For a chosen sample we obtained the following results for the refractive index n_1 and the thickness d_1: $n_1 = 1.817 \pm 0.05$ and $d_1 = (107.2 \pm 0.9)$ nm. The values of n_1 and d_1 of this sample were also determined by means of spectroscopic reflectometry. We found a very good agreement between the values of the corresponding parameters evaluated by means of both the optical methods mentioned.

2.2 Monochromatic immersion single angle of incidence method

This method can be called monochromatic immersion single angle of incidence (MISAI) ellipsometry too. Within this method the values of the ellipsometric parameters Ψ and Δ are measured for several non-absorbing ambients at one chosen angle of incidence and at one wavelength (as the non-absorbing ambients air and various non-absorbing liquids are used). If it is used a sufficient number of the liquids one can achieve the overdetermination of the problem, i. e., one can obtain the sufficient number of the values of the ellipsometric parameters allowing to evaluate the values of all the optical parameters characterizing the system under investigation in principle. This method was utilized for analyzing various single films in particular.

We utilized MISAI ellipsometry for the complete optical analysis of the native ox-ide layers taking place on GaAs-substrate (see Ref. [2]). However, we employed the modification of MISAI ellipsometry based on measuring and treating the values of the ellipsometric parameters of several samples of the system mentioned mutually differ-ing in the values of the thicknesses of the layers. The ellipsometric parameters were measured for the wavelength of 632.8 nm at the angle of incidence of 70.25°. As the immersion media air, acetone, toluene and carbon tetrachloride were used. Five sam-ples of the system mentioned above were measured under the experimental conditions described (the thicknesses of the native oxide layers of these samples were in the range 2-4 nm). The values of Ψ and Δ measured for the five samples were simultaneously treated by means of the least-squares method (LSM). The values of both the refractive index and thicknesses of the native oxide layers were determined with a sufficient accu-racy (e. g., $n_1 = 1.7 \pm 0.1$). Note, that by means of this method the authors mentioned determined the values of both the refractive index and extinction coefficient of the GaAs substrates with a high accuracy (it should be pointed out that the values of the optical constants of the GaAs substrates, the refractive index and the thicknesses of the native oxide layers were simultaneously determined within this method).

2.3 Monochromatic multiple angle of incidence method

Below this method will be call monochromatic multiple angle of incidence (MMAI) ellipsometry (in the literature this method is often called multiple angle of incidence (MAI) ellipsometry). MMAI ellipsometry is utilized for analyzing the thin film systems very frequently in practice. Within this method the angular dependences of the ellipso- metric parameters of the system studied are measured for a chosen wavelength in air. The treatment of the angular dependences of Ψ and Δ is mostly performed by the LSM.

We used MMAI ellipsometry for characterizing multilayer systems. This method was used for the determination of the values of the optical parameters of double and triple layers in particular. For example, the double layers formed by SiO_2 and Si_3N_4-films deposited on silicon single crystals substrate were analyzed by ellipsometry discussed in our paper [3]. ($\lambda = 632.8$ nm and $\theta_0 = 45$–$75°$). The values of the optical constants of the silicon substrate were taken from the literature (see Ref.[1]) and the values of four optical parameters describing the double layers, i. e., the values of n_1 and d_1 (the upper film) and n_2 and d_2 (the lower film), were evaluated using the LSM. In the paper it was shown that the accuracy of determining the values of the parameters mentioned was strongly dependent on the values of these parameters (especially on the values of both the thicknesses). For a chosen sample of the Si_3N_4/SiO_2 (the Si_3N_4 film is the upper one) and/or SiO_2/Si_3N_4 were achieved the following results: $n_1 = 2.015 \pm 0.004$, $d_1 = (104.7 \pm 0.2)$ nm, $n_2 = 1.439 \pm 0.002$ and $d_2 = (202.1 \pm 0.3)$ nm and/or $n_1 = 1.441 \pm 0.009$, $d_1 = (224 \pm 2)$ nm, $n_2 = 1.981 \pm 0.004$ and $d_2 = (94.0 \pm 0.2)$ nm. In this paper a samples of the three layer system $MgF_2/Si_3N_4/SiO_2$ on the silicon substrate were analyzed as well. For a chosen sample of this system the following results were obtained: $n_1 = 1.404 \pm 0.004$, $d_1 = (74.8 \pm 0.3)$ nm, $n_2 = 1.998 \pm 0.004$, $d_2 = (196.3 \pm 0.6)$ nm, $n_3 = 1.457 \pm 0.003$ and $d_3 = (109.1 \pm 0.3)$ nm. In the paper cited we showed that MMAI ellipsometry was very useful method for the complete optical analysis of the nonabsorbing double and triple layers if the thicknesses of the films forming the system are greater than about 50 nm.

2.4 Monochromatic immersion multiple angle of incidence method

This ellipsometric method can also be called monochromatic immersion multiple angle of incidence (MIMAI) ellipsometry. This modification of monochromatic ellipsometry is seldom utilized in practice. This is caused by the fact that its application is relatively difficult from the experimental point of view because special cells must be constructed.

For example, in our paper [4] we used the method discussed for the optical analysis of the system formed by the silicon substrate covered with the native oxide layer. For measuring the ellipsometric parameters of the system we utilized a special cell containing four windows corresponding to two different angles of incidence, i. e., $\theta_0 = 64.93°$ and 70.03°. Note that we also combined this method with MMAI ellipsometry at analysing the system mentioned.

2.5 Spectroscopic single angle of incidence method

During the last two decades methods of spectroscopic ellipsometry are utilized for the optical analysis of the thin film systems in an extensive way. The method of the optical analysis of the systems based on measuring the spectral dependences of Ψ and Δ of these systems at one angle of incidence can be called spectroscopic single angle of incidence (SSAI) ellipsometry. In the literature this method is often briefly called spectroscopic ellipsometry (SE).

There are two procedures of interpreting the spectral dependences of Ψ and Δ. By means of the first procedure the values of the pair of Ψ and Δ are treated for each wavelength separately. This means that in principle the treatment of the experimental data is the same as the treatment of those obtained by means of MSAI ellipsometry. Of course, in this way one can only determine the values of two parameters of the system studied for each wavelength.

The latter procedure is based on expressing the spectral dependences of the optical constants of the films studied by means of suitable dispersion formulae (e. g., by the Cauchy formula). Using the LSM the values of the parameters of these dispersion formulae together with the values of the thicknesses of the films are sought.

For example, we utilized SSAI ellipsometry for the complete optical analysis of many nonabsorbing and absorbing single layers. As an example of using this method for ana- lyzing the non-absorbing single layers our studies of silicon nitride single films deposited onto the Si-substrates can serve. The spectral dependences of the ellipsometric param- eters of the samples of the system mentioned were measured in the range 400–780 nm at the angle of incidence of 70°. The values of the optical constants of the substrates were again taken from the literature and the values of the thickness and the spectral dependences of the refractive index of the Si_3N_4-films were sought by the LSM (the spectral dependences of the refractive index of the films studied were assumed in the form of the Cauchy formula, i. e., it was assumed that $n_1 = A_1 + B_1/\lambda^2$). For a cho- sen sample following results were achieved: $A_1 = 1.99 \pm 0.04$, $B_1 = (2 \pm 1) \cdot 10^4$ nm^2 and $d_1 = (195 \pm 4)$ nm (the spectral dependence of the optical constants of the silicon substrate were fixed in the values published in Ref. [1]).

2.6 Spectroscopic multiple angle of incidence method

Within this ellipsometric technique the spectral dependences of the ellipsometric pa- rameters of the thin film system under investigation are measured at several angles of incidence. This means that this technique can be called spectroscopic multiple angle of incidence (SMAI) ellipsometry. In the literature the technique mentioned is often called variable angle of incidence spectroscopic ellipsometry (VASE). The interpretation of the experimental data achieved within SMAI ellipsometry can also be performed in two ways as in MMAI ellipsometry. Within the framework of the first way the angular dependences of Ψ and Δ are separately treated by means of a suitable numerical procedure at each wavelength of the spectral range of interest. Within the second one all the experimental data are interpreted simultaneously (i. e., the spectral dependences of Ψ and Δ measured for all the angles of incidence are treated together). Of course, in this case one must again assume concrete dispersion formulae expressing the spectral dependences of the optical constants of the materials forming the thin film system studied. It should be noted that during the last years a utilization of SMAI ellipsometry is enormous in the optical analysis of the thin film systems. This is caused by the fact that from the point of view of all the ellipsometric methods SMAI ellipsometry enables us to obtain the most detailed information concerning the optical properties of the systems analyzed.

We dealt with detailed studies of rough thin films by means of SMAI ellipsometry extensively. For example, we studied the SiO_2-films with the rough boundaries prepared by thermal oxidation of the rough surfaces of wafers of silicon single crystal (the rough silicon surfaces were produced using anodic oxidation of the smooth silicon surfaces and dissolution of anodic oxide films originated). The rough SiO_2-films prepared in this way can be approximated with the model of a nonabsorbing identical thin film (ITF) (see Ref. [5]). For interpreting the experimental data we used the RRT (see Ref. [6]) under assumption that the autocorrelation function is given by the Gaussian function. By using the LSM we then obtained the following results for the sample chosen: $\sigma = (8.29 \pm 0.10)$ nm, $T = (89 \pm 2)$ nm, $A_1 = 1.4473 \pm 0.0008$, $B_1 = (2.68 \pm 0.11) \cdot 10^3$ nm^2, $C_1 = (4.2 \pm 0.6) \cdot 10^7$ nm^4 and $d_1 = (287.5 \pm 0.2)$ nm (σ, T and C_1 denote the rms value of the heights irregularities and the autocorrelation length of the rough boundaries and the third constant of the Cauchy formula). Note that the ellipsometric parameters of the rough SiO_2-film were measured in the spectral range 240–830 nm at the angles of incidence $\theta_0 = 55$–$75°$. The propriety of the choice of model of the rough SiO_2-film used (i. e., the propriety of the ITF model) was supported by a good agreement both the experimental and theoretical data of Ψ and Δ. It should be noted that the experimental data were also treated by using the ideal model of the thin film (i. e., roughness of the boundaries was neglected). In this case we obtained the misrepresented spectral dependence of the refractive index n_1 of the SiO_2-film studied.

2.7 Combined ellipsometric methods

In practice one can encounter methods based on a combination of the methods of monochromatic ellipsometry presented above. By combining these methods of monochromatic ellipsometry it is possible to obtain a more extensive information about the thin film system studied. In the other words the combination of the methods mentioned enable us to remove or reduce a correlation between the optical parameters of the system sought. In the papers [7] and [4] the combination of MMAI ellipsometry with MISAI ellipsometry was used to analyze the native oxide layers on the surfaces of single crystals of Si, GaAs and Ge. The angular dependences of Ψ and Δ of the samples of these systems were thus measured for the wavelength of 632.8 nm in the range 45–80° in air. Moreover, for the same wavelength the values of the ellipsometric parameters of the same samples were measured for various immersion liquids at one angle incidence

(in the paper [7] and/or [4] the angle of 70.03° and distilled water and toluene and/or the angle of 70.25° and distilled water, toluene, acetone and carbon tetrachloride were employed as the angle of incidence and immersion liquids at applying MISAI ellipsometry). Within the combined method of MMAI and MISAI ellipsometry the angular dependences of Ψ and Δ measured in air and the dependences of Ψ and Δ measured at one angle of incidence in the immersion liquids were simultaneously treated by the LSM for every sample under investigation. Note that the values of the refractive indices of the immersion liquids were again measured in the independent way (for details see, for example, the paper [4]). It was found that by using this combined method one could not determine the values of all the optical parameters characterizing the samples analyzed, i. e., the values of both the refractive indices of the substrate and native oxide layer, the thickness of this layer and the extinction coefficient of the substrate (this fact was evidently caused by a correlation of the parameters mentioned). However, in the paper cited it was shown that it was possible to determine the values of both the refractive indices and the thickness of the layer of all the samples studied with a sufficient accuracy if the values of the extinction coefficient of the substrates, i. e., Si, GaAs and Ge, had been considered as the known quantity taken from the literature. It was thus assumed that the values of the extinction coefficients of Si, GaAs and Ge laid within the intervals $k = 0.02 \pm 0.01$, $k = 0.25 \pm 0.05$ and $k = 0.815 \pm 0.025$, respectively. By means of this combined method the following results were achieved for a chosen samples of the systems specified above: $n_1 = 1.53 \pm 0.02$, $d_1 = (3.3 \pm 0.1)$ nm and $n = 3.879 \pm 0.003$ (NOL/Si), $n_1 = 1.63 \pm 0.07$, $d_1 = (3.8 \pm 0.5)$ nm and $n = 3.862 \pm 0.007$ (NOL/GaAs) and $n_1 = 1.43 \pm 0.08$, $d_1 = (5 \pm 2)$ nm and $n = 5.42 \pm 0.08$ (NOL/Ge). The symbol NOL denotes the native oxide layer.

2.8 Combination of the ellipsometric methods with the other optical methods

In practice a combination of the ellipsometric methods with the other optical ones appears to be very powerful. In several papers it was shown that this combination allowed to decrease the correlation between searched parameters of thin film systems under investigation and it thus allowed to analyze the systems described with a greater number of the parameters (e. g., the thin film systems exhibiting various defects).

The combined method of SMAI ellipsometry and spectroscopic reflectometry was also employed for characterizing the NOL taking place on slightly rough surfaces of silicon single crystal in the paper [8]. However, this combined method was applied in the modification based on the simultaneous treatment of the experimental data obtained for all the samples under investigation. This means that by means of the LSM the experimental data corresponding to SMAI ellipsometry and spectroscopic reflectometry obtained for all the samples were treated together. The authors of the paper mentioned analyzed one smooth surface and the three differently rough surfaces of silicon wafers. It should be noted that the relative reflectances of the rough samples owing to the smooth sample at near-normal incidence were measured and interpreted. The rough silicon surfaces were again prepared by the procedure consists of anodic oxidation of the smooth surfaces and following dissolution of anodic oxide films originated by this anodic

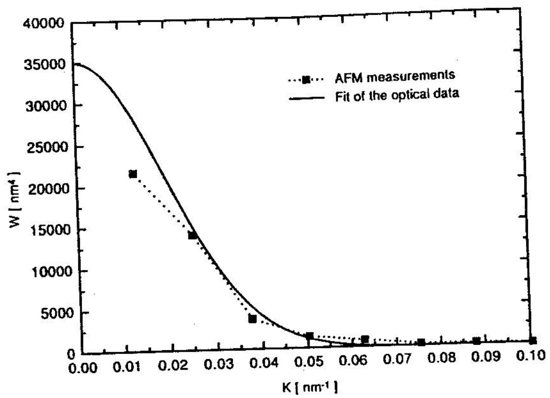

Fig. 1. Comparison of the spectral density of the spatial frequency of roughness determined by the optical method and AFM.

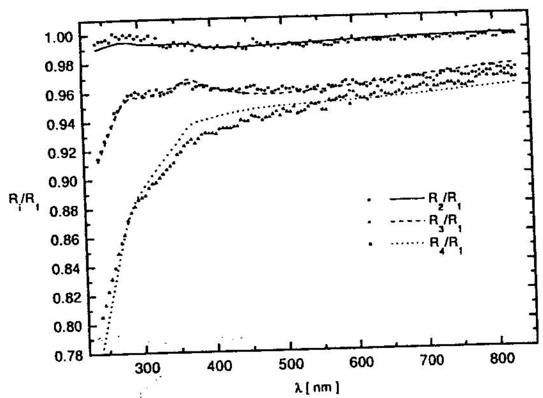

Fig. 2. The spectral dependences of the relatives reflectances of the rough samples owing to the smooth one (the points and/or curves denote the experimental and/or theoretical data).

oxidation. Before the measurements the smooth Si-surface was placed into the dissolving solution together with the rough Si-surfaces so that one could assume that all the NOLs existing on the smooth and slightly rough surfaces exhibited the same values of both the thicknesses and refractive index. The parameters of roughness of the boundaries of the individual NOLs were mutually different (this fact was caused by different conditions of anodic oxidation). The interpretation of the experimental data was simplified by the fact that the spectral dependences of the optical constants of the silicon substrate and

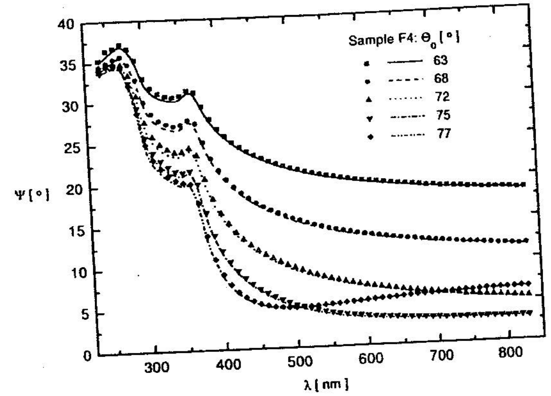

Fig. 3. The spectral dependences of Ψ of the roughest sample F4 (the points and/or curves denote the experimental and/or theoretical data).

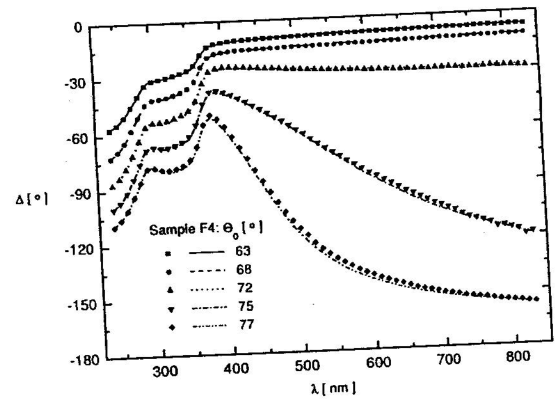

Fig. 4. The spectral dependences of Δ of the roughest sample F4 (the points and/or curves denote the experimental and/or theoretical data).

the spectral dependence of the refractive index of the NOL or all the samples were fixed in the dependences taken from the literature (it was assumed that the refractive index of the NOL was identical with the refractive index of amorphous SiO_2). For interpreting the experimental data of the rough samples the formulae corresponding to RRT were utilized. By means of the described procedure of interpreting the experimental data the following results were achieved: $d_1 = (2.70 \pm 0.04)$ nm, $\sigma_2 = (2.15 \pm 0.06)$ nm, $T_2 = (29 \pm 2)$ nm, $\sigma_3 = (6.16 \pm 0.02)$ nm, $T_3 = (47.6 \pm 0.3)$ nm, $\sigma_4 = (9.03 \pm 0.01)$ nm and $T_4 = (73.4 \pm 0.3)$ nm. The symbols σ_2 and T_2, σ_3 and T_3 and σ_4 and T_4 denote the rms value and autocorrelation length of the first, second and third rough samples, respectively. A correctness of the results presented was supported by the agreement achieved in the values of the quantities characterizing roughness of the roughest sample by AFM and the optical combined method discussed. In the paper this agreement was illustrated using the comparison of the values of the spectral density of the spatial frequencies of roughness W determined by the optical method and AFM see fig. 1.

Note that within the optical method the spectral density W could easily be calculated by means of the values of σ and T found because the Gaussian form of this quantity was assumed in the paper. The results obtained by the combined optical method was also supported by an agreement between the experimental and theoretical data corresponding to this method (see figs. 2, 3 and 4).

3 Conclusion

In this paper the brief review of the ellipsometric methods used in practice has been presented. Attention has been paid to the practical features of these methods (i.e., the accuracy and reliability of the methods have been illustrated by means of the examples of the ellipsometric analysis of some thin film systems chosen). Moreover, in this paper it has been shown that the ellipsometric methods discussed are powerful and efficient for the optical analysis of many various systems of thin films. It should be noted that theoretical formulae needed for applying the methods presented are introduced in various monographs and review articles (see, for example, the monograph of Vašíček [9] or the review paper of Ohlídal and Franta [10]).

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References

[1] D. E. Aspnes, A. A. Studna: *Phys. Rev.* B **27** (1983), 985.

[2] I. Ohlídal, M. Líbezný: *Surf. Interface Anal.* **17** (1991), 171

[3] A. Paneva, I. Ohlídal: *Thin Solid Films* **145** (1986), 23

[4] I. Ohlídal, M. Líbezný: *Surf. Interface Anal.* **16** (1990), 46

[5] I. Ohlídal, K. Navrátil, F. Lukeš: *J. Opt. Soc. Am.* **61** (1971), 1630

[6] D. Franta, I. Ohlídal: *J. Mod. Opt.* **45** (1998), 903.

[7] I. Ohlídal, F. Lukeš: *Appl. Surf. Sci.* **35** (1988-89), 259.

[8] I. Ohlídal, D. Franta, B. Rezek, M. Ohlídal: in *Proc. Conf. ECASIA 97 - 7th European Conference on Applications of Surface and Interface Analysis*, Göteborg, 1997 (eds. I. Olefjord, L. Nyborg and D. Briggs). Wiley, Chichester 1997, p. 1051

[9] A. Vašíček: *Optics of Thin Films*, North-Holand, Amsterdam 1960.

[10] I. Ohlídal, D. Franta: in: *Progress in Optics* (ed. E. Wolf). North-Holand, Amsterdam (in print).