acta physica slovaca vol. 50 No. 4, 411 – 421 August 2000

ANALYSIS OF THIN FILMS BY OPTICAL MULTI-SAMPLE METHODS[*]

D. Franta[ab], I. Ohlídal[ab]
(a) Department of Physical Electronics, Faculty of Science, Masaryk University,
Kotlářská 2, 611 37 Brno, Czech Republic
(b) Joint Laboratory of Modern Metrology of Faculty of Science of Masaryk University,
Czech Metrology Institute and Faculty of Mechanical Engineering of Technical
University of Brno, Kotlářská 2, 611 37 Brno, Czech Republic

Received 28 June 2000, accepted 30 June 2000

In this paper a brief review of the optical methods based on the simultaneous interpretation of the different optical experimental data obtained for thin film systems is presented. These methods are known as the multi-sample methods. It is shown that these optical multi-sample methods are very useful for analyzing many thin film systems. In particular it is illustrated that selected optical multi-sample methods are powerful for studying the following problems: investigations of growing the native oxide layers on the semiconductor surfaces; suppression of the influence of the transition interlayers between the substrates and thin films and determination of the optical constants of bulk materials. Concrete experimental examples demonstrating the foregoing statements are presented in this paper as well.

PACS: 78.20.Bh, 78.20.Ci, 78.66.-w

1 Introduction

In practice thin films are often analyzed using the optical methods. Ellipsometry and reflectometry belong to the most important optical methods appropriated for this analysis. The ellipsometric and reflectometry methods published in the literature are mostly based on interpreting the experimental data corresponding to one sample of a thin film system studied (these methods can be called the single-sample methods). In the last years several optical methods based on simultaneous treatment of the experimental data of several samples of the thin film system under investigation were published. These methods are called the multi-sample methods.

In this contribution a review of applications of the multi-sample methods for the optical characterization of thin film systems will be presented. It will be shown that the optical multi-sample methods have important advantages in comparison with the single-sample methods.

The optical multi-sample methods can especially be used to solve the following problems:

1. Investigations of subtle effects concerning thin films (e. g. growth of native oxide layer on the surfaces of the solids, investigation of slight roughness of the boundaries etc.).

---

[*] Presented at the Workshop on Solid State Surfaces and Interfaces II, Bratislava, Slovakia, June 20 – 22, 2000.

2. Suppression of the influence of complicated defects of the thin film systems at their analysis (e. g. existence of transition interlayers etc.).

3. Determination of the optical constants of bulk materials whose ideal surfaces can not be prepared (e. g. for materials whose surfaces are covered with native oxide layers etc.).

In this contribution it will also be shown that the combination of variable angle of incidence spectroscopic ellipsometry and near-normal incidence spectroscopic reflectometry is especially useful for applying the optical multi-sample methods.

2 Principle of the methods

The basic idea of these multi-sample methods consists in the fact that the samples of the system, whose optical quantities are measured, have to exhibit some parameters with the identical values. This fact enable us to reduce the number of the parameters searched which causes a decrease of the correlations between these parameters. The decrease of the correlations then implies the increase of both the reliability and precision of the results achieved within the multi-sample methods.

3 Examples

In this section the typical examples of the applications of some modifications of the multi-sample methods will be presented. The attention will be devoted to the examples important from the practical point of view.

3.1 Growth of native oxide layers

It is known that it is very difficult to determine the values of the optical parameters, i. e. the values of the thickness and refractive index, characterizing the native oxide layers (NOL) originating on the surfaces of various solids. It is also known that ellipsometric methods are very sensitive to the existence of the NOL. Of course, this fact does not involve that all the ellipsometric methods enable us to analyze the layers mentioned automatically.

It was found that the ellipsometric method based on interpreting the ellipsometric parameters measured for several angles of incidence (multiple angle of incidence method) at a chosen wavelength did not allow to determine the values of both the optical parameters of the NOL [1]. This is caused by the fact that the values of the thicknesses of these layers are small (the values of the these thicknesses are equal to several nanometers) which implies a strong correlation between the optical parameters sought. This correlation causes great uncertainties of both the parameters mentioned.

In paper [2] it was shown that the use of immersion multiple angle of incidence (IMAI) ellipsometry[1] allowed to reduce the correlation between the parameters of the NOL placed on

---

[1] Within IMAI ellipsometry the ellipsometric parameters are measured as functions of the angle of incidence and the refractive index of the ambient.

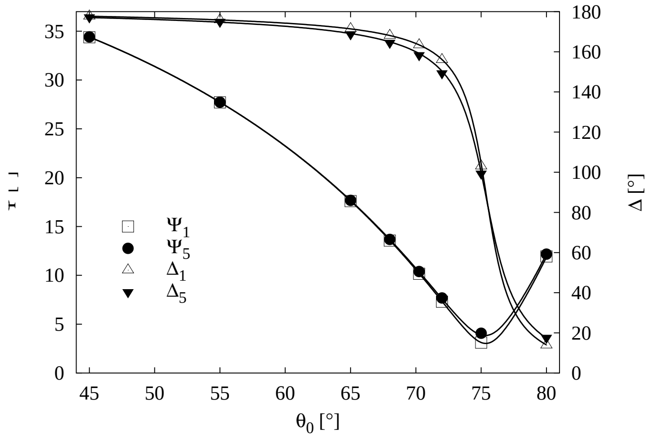

Fig. 1. The angular dependences of the ellipsometric parameters Ψ and Δ for two chosen samples with thicknesses $d_{1,1} = 2.27$ nm and $d_{1,5} = 3.59$ nm. The points and/or curves denotes the experimental and/or theoretical values of the quantity mentioned.

semiconductor surfaces (Si, GaAs and Ge). In consequence of this fact the values of the thickness and the refractive index of the NOL could be determined with a sufficient accuracy under assumption that the extinction coefficient of the substrate was evaluated in an independent way.

Only the use of the multi-sample modification of IMAI ellipsometry enables us to determine the values of the optical parameters of the NOL and the values of the refractive index and extinction coefficient of the semiconductor substrate with a sufficient accuracy [3]. In paper [3] the growth of the NOL on the GaAs surface was studied under normal laboratory conditions. Within this study the ellipsometric parameters of five samples of the system NOL/GaAs were measured (a monochromatic ellipsometer working for a wavelength of 632.8 nm was used for this purpose). The corresponding ellipsometric dependences for two chosen samples are introduced in Figs. 1 and 2. The values of the thicknesses $d_{1,1}, \ldots d_{1,5}$ of the NOL corresponding to these samples were mutually different (the sample surfaces were exposed to the laboratory atmosphere for different periods). It was assumed that from the physical point of view the samples of the system NOL/GaAs corresponded to the model of homogeneous isotropic non-absorbing thin films placed on the homogeneous isotropic absorbing substrate with the smooth boundaries. Further it was assumed that the values of the refractive index of the NOL were identical for all the samples under investigation. The experimental data of all the five samples were simultaneously treated by a least-squares method (LSM). In this way the values of the refractive index of the GaAs substrate n, the extinction coefficient of this substrate k, the refractive index n_1 of all the NOL and the thicknesses of the individual NOL, i. e. $d_{1,1}, \ldots d_{1,5}$, were determined as follows: $n = 3.8372 \pm 0.0015$, $k = 0.204 \pm 0.009$, $n_1 = 1.64 \pm 0.02$, $d_{1,1} = (2.27 \pm 0.10)$ nm, $d_{1,2} = (2.66 \pm 0.10)$ nm, $d_{1,3} = (3.05 \pm 0.09)$ nm, $d_{1,4} = (3.41 \pm 0.09)$ nm and $d_{1,5} = (3.59 \pm 0.09)$ nm. From the foregoing results one can see that the values of all the optical parameters characterizing all the samples of the system NOL/GaAs were determined with the high accuracy. The reliability of the results mentioned is supported by the two following facts:

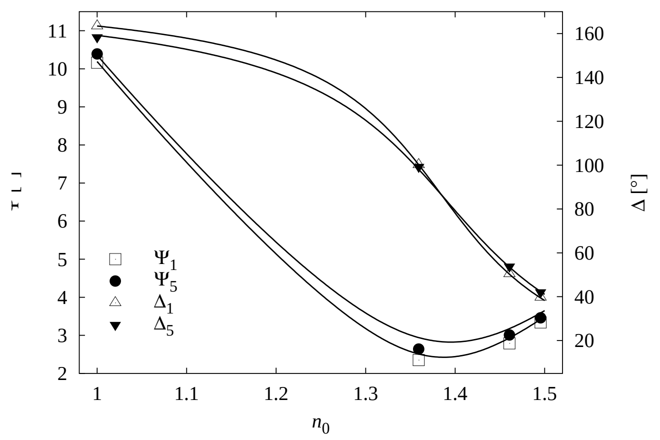

Fig. 2. The dependences of the ellipsometric parameters Ψ and Δ on the refractive index of ambient for two chosen samples with thicknesses $d_{1,1} = 2.27$ nm and $d_{1,5} = 3.59$ nm. The points and/or curves denotes the experimental and/or theoretical values of the quantity mentioned.

- The values of both the refractive index and extinction coefficient of the GaAs substrate agree with those determined using the other methods by the other researchers very well (see e. g. [4, 5]).
- The dependence of the values of the thickness of the NOL on time (curve of the growth) determined using this method corresponds to the logarithmic law

  $$d(t) = a_0 + b_0 \ln(t + t_0) \tag{1}$$

  which agrees with the theory of oxidation of GaAs (see Fig. 3).

It is evident that one can employ the multi-sample method described in this section for characterizing the native oxide layers growing on the other semiconductor surfaces.

3.2 Suppression of the influence of defects

In practice it is often necessary to analyze the thin film systems exhibiting various defects. The situation is especially difficult if the systems with complicated structures have defects. In this case one must find the values of a great number of the parameters characterizing these systems. It is known that the optical single-sample methods can not mostly be used to perform the complete optical analysis of such the thin film systems. It should be noted that one can often obtain a good agreement between both the theoretical and experimental data at the optical analysis if within the optical single-sample methods models are used that do not respect these defects. Of course, in spite of this good agreement the values of the parameters of the systems found are evidently wrong. In general the optical multi-sample methods are more resistant against the influence of the defects if these defects are not included into the models employed for analyzing.

The foregoing statements can be illustrated using the optical analysis of diamond like carbon (DLC) films created onto silicon substrates. In paper [6] a comparison of the results achieved

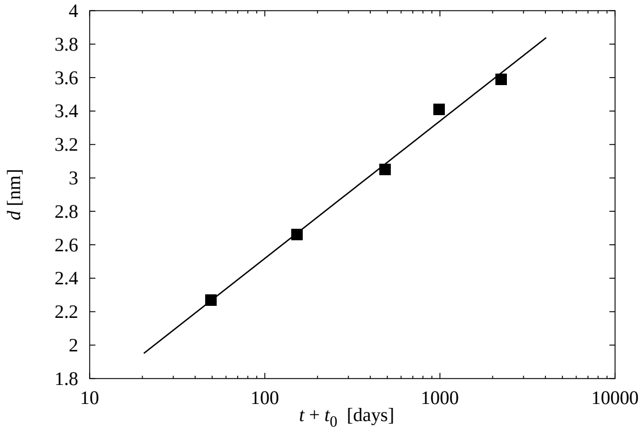

Fig. 3. Logarithmic dependence of the thickness of the NOL of GaAs on time ($a_0 = 0.88 \pm 0.21$ nm, $b_0 = 0.357 \pm 0.031$ nm and $t_0 = 46 \pm 16$ days, see Eq. (1)).

within the optical analysis of the DLC films by the single-sample method on one hand and multi-sample method on the other hand is presented. Six samples of the DLC films were prepared by plasma enhanced chemical vapor deposition (PECVD). The individual samples differ in time of the deposition and therefore the thicknesses of these samples were mutually different. The main aim of the optical studies of the DLC films mentioned consisted in investigating a homogeneity of these films along their thicknesses. If the single-sample modification of variable angle of incidence spectroscopic ellipsometry (VASE)[2] was employed surprising results concerning the refractive index of the DLC films studied were obtained even when the good agreement between both the theoretical and experimental data was achieved (the model of the isotropic homogeneous absorbing thin film placed on isotropic homogeneous absorbing substrate with the smooth boundaries was used at the analysis). The peculiar behavior of the refractive index of the DLC films consists in depending this quantity on the deposition time (see Fig. 4). Note that this behavior of the refractive index was reproducible. It should also be emphasized that the spectral dependences of both the optical constants of the silicon substrate had to be fixed in the values taken from the literature. Within the single-sample method it was impossible to determine these spectral dependences together with the optical parameters characterizing the DLC films because of the existence of the correlation between the parameters sought.

In paper [6] it was shown that the multi-sample method based on VASE allowed to determine the correct values of the optical parameters of the DLC films together with the values of the optical constants of the substrates. This was caused by the fact that the correlation between the parameters sought (including the substrate optical constants) was considerably reduced. Within this multi-sample method the model identical with that employed in the single-sample method was used. However, it was found that this model was not correct. Using XPS[3] it was found that a transition interlayer took place in the boundary between the DLC film and silicon single crystal substrate. This transition layer exhibited a composed structure originated by an implantation

---

[2] Within VASE the ellipsometric parameters are measured as functions of the angle of incidence and wavelength.

[3] X-ray photoelectron spectroscopy

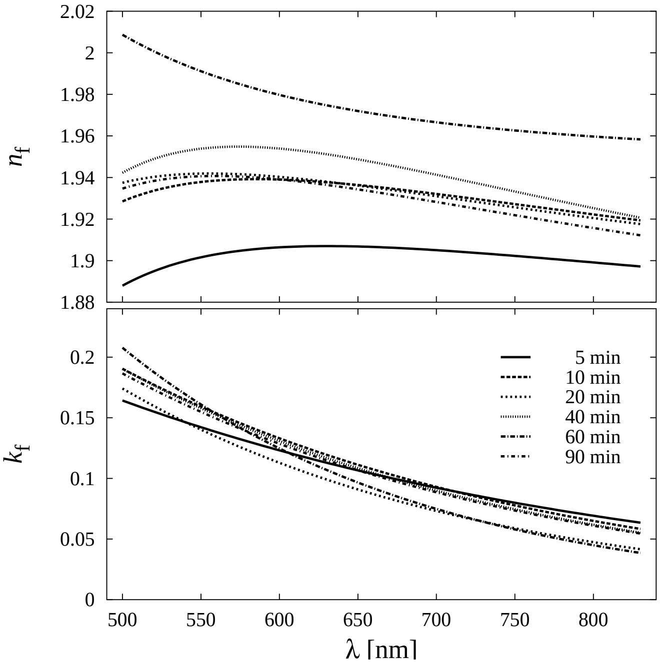

Fig. 4. Spectral dependences of refractive index n_f and extinction coefficient k_f of the individual samples of the DLC films determined using the single-sample method (deposition times are introduced as well).

of carbon ions into the surface of silicon single crystal covered by the NOL in the beginning of the deposition process. In spite of neglecting this transition layer in the model used within the multi-sample method the values of the optical parameters of the DLC films were not influenced with this fact. The last statement was proved by modeling the DLC optical constants by means of a relatively complicated dispersion model [7] fulfilling the Kramers–Krönig relations (see Fig. 5). The optical constants of the substrates evaluated using the multi-sample method described differed from those corresponding to silicon single crystal. These optical constants represent a certain effective ones corresponding to the substrate and transition layer.

3.3 Determination of the optical constants of bulk materials

Our experiences imply that the use of the multi-sample method based on combining VASE and near normal incidence spectral reflectometry (NNSR) is very useful. The advantage of the ellipsometric techniques consists in the fact that within these techniques the absolute intensity values are not measured. Within NNSR the spectral dependences of the absolute reflectances of the samples are often measured using chosen standards their reflectances are known. Of course, it is very problematic to determine the correct values of the reflectances of the standards which decreases both the correctness and accuracy of the absolute reflectances of the samples measured. The advantage of the multi-sample methods mentioned in this section consists in measuring the mutual relative reflectances of the sample family of the system studied.

The multi-sample method mentioned was used to determine the spectral dependences of the

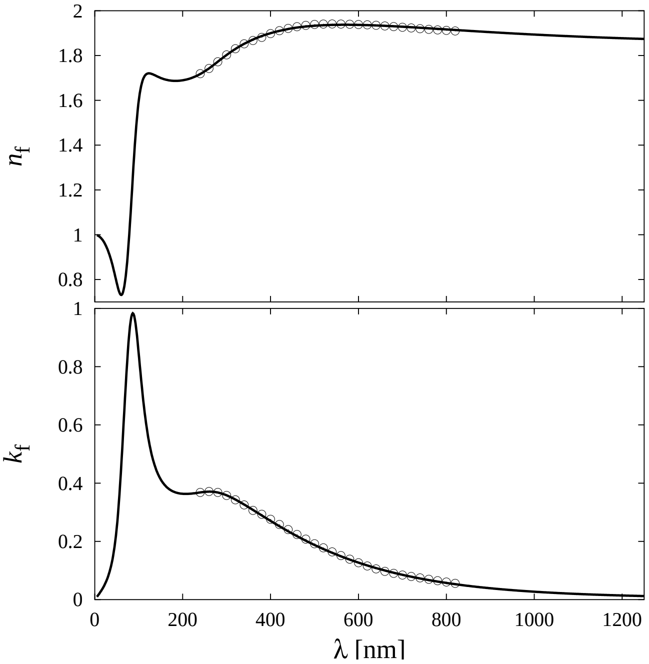

Fig. 5. Spectral dependences of refractive index $n_{\rm f}$ and extinction coefficient $k_{\rm f}$ of the DLC films determined using the multi-sample method (points). The curves denote the data obtained using the model fulfilling the Kramers–Krönig relations mentioned in the text.

optical constants of the system formed by the thermal SiO_2 film and silicon single crystal substrate [8]. The main aim of this study was to determine the spectral dependences of both the optical constants of the silicon substrate. For this purpose six samples of the system mentioned were investigated. The individual samples differed with each other in the values of their thicknesses (15–100 nm).

The ellipsometric parameters Ψ and Δ and the reflectance R of isotropic thin film systems are defined as follows:

$$\tan\Psi\,\mathrm{e}^{\mathrm{i}\Delta} = \frac{\hat{r}_p}{\hat{r}_s}, \quad R = \frac{|\hat{r}_p|^2 + |\hat{r}_s|^2}{2}, \tag{2}$$

where $\hat{r}_p$ and/or $\hat{r}_s$ denotes the reflection Fresnel coefficient for p and/or s-polarization. It is reasonable to introduce the complex quantities $\hat{\rho}_{ij}$ defined by these equations:

$$\hat{\rho}_{ii} = \tan\Psi_i\,\mathrm{e}^{\mathrm{i}\Delta_i}, \quad \hat{\rho}_{ij} = \frac{R_i}{R_j} + \mathrm{i}\frac{R_j}{R_i}, \tag{3}$$

where the indices i and j express the numbers of the samples ($i, j = 1, 2 \ldots, 6$). For finding the values of the parameters characterizing the samples the LSM can be utilized. One can then construct the following merit function:

$$S(\vec{X}) = \sum_k |\hat{\rho}_{ij}(\vec{X}, \lambda_k, \theta_{0k}) - \hat{\rho}_k^{\rm exp}|^2 w_k, \tag{4}$$

where $\vec{X}$ denotes the vector whose components are identical with the parameters sought. The index k represents the serial number of the experimental values of the complex quantity $\hat{\rho}_k^{\mathrm{exp}}$, w_k are the weights of the experimental values and λ_k and/or θ_{0k} is the wavelength and/or the angle of incidence of light falling onto the upper boundary of the system SiO$_2$/Si belonging to the corresponding experimental value (the indices i and j are functions of the index k). The function $\hat{\rho}_{ij}(\vec{X}, \lambda_k, \theta_{0k})$ is calculated using Eqs. (2) and (3). The values of the parameters sought corresponding to the minimum of the function $S(\vec{X})$ are considered to be the true values of these parameters characterizing the samples studied. In the procedure of searching the minimum of S the Marquardt–Levenberg algorithm was used [9].

The spectral dependences of the optical constants of the silicon single crystal substrate determined using the multi-sample method described are tabulated in Table 1.

The spectral dependence of the refractive index of the SiO$_2$ films simultaneously evaluated agreed with that presented for amorphous SiO$_2$ in the literature. In paper [8] it was also shown that the samples of the system SiO$_2$/Si corresponded to the physical model formed by isotropic homogeneous non-absorbing thin film and isotropic homogeneous absorbing substrate with sufficient accuracy. Thus it was shown that it was not necessary to consider a transition interlayer between the silicon substrate and SiO$_2$ film as presented by the other researchers in the literature (e. g. [10]).

The optical multi-sample method presented in this section can evidently be used to analyze the other systems formed by a semiconductor substrate covered with a non-absorbing thin films.

4 Conclusion

In this paper the brief review of the optical multi-sample methods suitable for analyzing the thin film system was presented. It was shown that these multi-sample methods are more powerful for analyzing the systems mentioned in comparison with the single-sample methods. This fact is caused by reducing the correlation between the parameters sought within the multi-sample methods. In particular it was demonstrated that these multi-sample methods were useful for the following studies:

1. Investigations of growing the native oxide layers on the semiconductor surfaces.
2. Suppression of the influence of the transition interlayers between the substrates and thin films.
3. Determination of the optical constants of bulk materials.

It may be expected that the optical multi-sample methods will be very perspective for analyzing various thin film systems in the near future.

Acknowledgment We wish to thank to researchers of SCB of the Masaryk University for their help concerning numerical computations. The present work was supported by the Grant Agency of the Czech Republic, contracts 106/96/K245 and 202/98/0988, and by the Ministry of Education, contract VS96084.

Table 1. The values of the refractive index n and extinction coefficient k of silicon single crystal.

nm	cm^{-1}	eV	n	k
240	41667	5.166	1.668	3.448
245	40816	5.061	1.640	3.539
250	40000	4.959	1.632	3.671
255	39216	4.862	1.657	3.848
260	38462	4.769	1.717	4.076
265	37736	4.679	1.820	4.353
270	37037	4.592	2.008	4.684
275	36364	4.509	2.352	5.018
280	35714	4.428	2.832	5.268
285	35088	4.350	3.415	5.448
290	34483	4.275	4.232	5.389
295	33898	4.203	4.815	4.840
300	33333	4.133	4.994	4.308
305	32787	4.065	5.026	3.934
310	32258	4.000	5.024	3.673
315	31746	3.936	5.021	3.489
320	31250	3.875	5.030	3.358
325	30769	3.815	5.057	3.255
330	30303	3.757	5.096	3.165
335	29851	3.701	5.147	3.091
340	29412	3.647	5.208	3.034
345	28986	3.594	5.283	3.003
350	28571	3.542	5.389	3.010
355	28169	3.493	5.573	3.056
360	27778	3.444	5.952	3.085
365	27397	3.397	6.510	2.850
370	27027	3.351	6.898	2.216
375	26667	3.306	6.875	1.497
380	26316	3.263	6.599	1.004
385	25974	3.220	6.293	0.720
390	25641	3.179	6.025	0.549
395	25316	3.139	5.817	0.444
400	25000	3.100	5.642	0.373
405	24691	3.061	5.488	0.318
410	24390	3.024	5.352	0.277
415	24096	2.988	5.237	0.244
420	23810	2.952	5.136	0.220
425	23529	2.917	5.047	0.199
430	23256	2.883	4.965	0.183
435	22989	2.850	4.888	0.168
440	22727	2.818	4.817	0.153
445	22472	2.786	4.757	0.142
450	22222	2.755	4.700	0.134
455	21978	2.725	4.650	0.125

(continued)

nm	cm^{-1}	eV	n	k
460	21739	2.695	4.599	0.117
465	21505	2.666	4.553	0.111
470	21277	2.638	4.513	0.104
475	21053	2.610	4.478	0.099
480	20833	2.583	4.440	0.093
485	20619	2.556	4.405	0.087
490	20408	2.530	4.370	0.081
495	20202	2.505	4.342	0.077
500	20000	2.480	4.316	0.070
505	19802	2.455	4.290	0.064
510	19608	2.431	4.257	0.071
515	19417	2.407	4.234	0.068
520	19231	2.384	4.212	0.064
525	19048	2.362	4.191	0.062
530	18868	2.339	4.170	0.059
535	18692	2.317	4.147	0.058
540	18519	2.296	4.128	0.055
545	18349	2.275	4.110	0.052
550	18182	2.254	4.093	0.051
555	18018	2.234	4.076	0.048
560	17857	2.214	4.058	0.048
565	17699	2.194	4.042	0.045
570	17544	2.175	4.028	0.044
575	17391	2.156	4.014	0.041
580	17241	2.138	3.999	0.040
585	17094	2.119	3.986	0.038
590	16949	2.101	3.972	0.036
595	16807	2.084	3.960	0.033
600	16667	2.066	3.949	0.032
605	16529	2.049	3.938	0.030
610	16393	2.033	3.927	0.028
615	16260	2.016	3.916	0.027
620	16129	2.000	3.907	0.027
625	16000	1.984	3.897	0.026
630	15873	1.968	3.888	0.025
635	15748	1.953	3.878	0.024
640	15625	1.937	3.869	0.023
645	15504	1.922	3.860	0.022
650	15385	1.907	3.852	0.022
655	15267	1.893	3.844	0.021
660	15152	1.879	3.836	0.021
665	15038	1.864	3.828	0.020
670	14925	1.851	3.821	0.020
675	14815	1.837	3.814	0.020
680	14706	1.823	3.807	0.019

(continued)

nm	cm^{-1}	eV	n	k
685	14599	1.810	3.800	0.019
690	14493	1.797	3.794	0.019
695	14388	1.784	3.787	0.018
700	14286	1.771	3.781	0.018
705	14184	1.759	3.775	0.019
710	14085	1.746	3.769	0.018
715	13986	1.734	3.764	0.017
720	13889	1.722	3.758	0.018
725	13793	1.710	3.753	0.018
730	13699	1.698	3.748	0.017
735	13605	1.687	3.742	0.017
740	13514	1.675	3.737	0.017
745	13423	1.664	3.732	0.017
750	13333	1.653	3.727	0.017
755	13245	1.642	3.723	0.016
760	13158	1.631	3.718	0.016
765	13072	1.621	3.715	0.015
770	12987	1.610	3.710	0.015
775	12903	1.600	3.705	0.015
780	12821	1.590	3.701	0.015
785	12739	1.579	3.697	0.015
790	12658	1.569	3.694	0.014
795	12579	1.560	3.690	0.014
800	12500	1.550	3.686	0.014
805	12422	1.540	3.683	0.014
810	12346	1.531	3.680	0.013
815	12270	1.521	3.677	0.013
820	12195	1.512	3.673	0.012
825	12121	1.503	3.669	0.012
830	12048	1.494	3.666	0.012

References

[1] M. M. Ibrahim, N. M. Bashara: *J. Opt. Soc. Am.* **61** (1971) 1622

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

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

[4] F. Lukeš: *Optik* **31** (1970) 83

[5] H. W. Dinges: *J. Phys.* **44** (1983) C10

[6] D. Franta, L. Zajíčková, I. Ohlídal, J. Janča, K. Veltruská: *Thin Solid Films*, submitted

[7] D. Franta, I. Ohlídal, D. Munzar: *Acta Phys. Slov.* **48** (1998) 451

[8] I. Ohlídal, D. Franta, E. Pinčík, M. Ohlídal: *Surf. Interface Anal.* **28** (1999) 240

[9] W. D. Marquardt: *J. Soc. Ind. Appl. Math.* **11** (1963) 431

[10] C. M. Herzinger, B. Johs, W. A. McGahan, J. A. Woollam, W. Paulson: *J. Appl. Phys.* **83** (1998) 3323