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## METHOD FOR DETERMINING OPTICAL CONSTANTS AND THE THICKNESS OF THE THIN FILM

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Here are presented the results of the development and application of methods for determining the optical constants and thickness of thin films. The generalized target model function is formed to determine the unmeasured parameters. The model is applied by using the least squares method and the steepest descent. Increased efficiency is achieved by using a three-step processing algorithm. The proposed method was applied to calculate the characteristics of the multi-alkali photocathode, which is a complex compound having in its composition antimonides of potassium, sodium and cesium. A comparison of the calculation results with the data given in the literature is presented. Refs 11. Figs 4.

*Keywords:* thin film, optical constants, the thickness of the thin film, the generalized target model function, the data processing algorithm.

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## МЕТОДИКА ОПРЕДЕЛЕНИЯ ОПТИЧЕСКИХ КОНСТАНТ И ТОЛЩИНЫ ТОНКОЙ ПЛЕНКИ

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Представлены результаты разработки и применения методики определения оптических констант и толщины тонкой пленки. Для определения неизмеримых параметров сформирована обобщенная целевая модельная функция. Модельная привязка осуществляется с помощью методов наименьших квадратов и наискорейшего спуска. Повышение эффективности достигается путем применения трехэтапного алгоритма обработки данных. Предложенная методика применена для расчета характеристик многощелочного фотокаатода — сложного соединения, имеющего в своем составе антимиониды калия, натрия и цезия. Проведено сравнение результатов расчетов с данными, приводимыми в литературе. Библиогр. 11 назв. Ил. 4.

*Ключевые слова:* тонкая пленка, оптические константы, толщина тонкой пленки, обобщенная целевая модельная функция, алгоритм обработки данных.

**Introduction.** There are three groups of methods for simultaneous determination of the optical constants of the material and the thickness of its layer. The first group is based on the use of the Kramers—Kronig relations. In this case it is only possible to measure the two parameters to determine the three unknown [1, 2]. The missing equation is replaced by an integral relation of the

$$\varepsilon_1(\omega) = 1 + \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\varepsilon_2(x)}{x - \omega} dx,$$

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$$\varepsilon_2(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\varepsilon_1(x) - 1}{x - \omega} dx,$$

where  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  — the real and imaginary parts of the complex permittivity. In this case formally you need to know the measured values in an infinite range of wavelengths. However, due to known physical laws, it is sufficient to carry out measurements in a limited, but sufficiently wide spectral range. And then the obtained values are extrapolated to infinite frequency values according to any relatively simple law, for example, exponential law. Such methods have been used in particular in [3]. We think that this method is not satisfactory.

Indeed, real structures are adsorbed onto a substrate. Its optical characteristics can not be assumed to be known in any broad spectral range. Suffice it to say that a normal glass is transparent in the wavelength range from 500 to 2700 nm, and in the range of 360–500 nm absorption is significantly affected. However, you can conditionally put a lower bound equal to 360 nm or even lower it to 320 nm. The range of our interest is rather narrow. It is also known that in the region less than 300 nm, most materials have a complicated structure of the optical spectra. This makes the extrapolation using some simple functions rather doubtful.

The second group of methods is based on an approximation of the refractive index depending on the wavelength by using any suitable function, and further fitting the measured transmittance depending on the wavelength to determine the refractive index [4]. In practice, this group of methods does not provide a satisfactory approach in any circumstances except for some numbers of relatively studied materials, which only requires some fitting (adjustment) of parameters to take into account the nuances of the technological manufacturing.

The third group of methods is based on the measurement of any of three values, depending on the optical constants of the investigated film, which makes it possible to solve the corresponding system of equations. In this case the choice of measured values becomes relevant. It can be any available three measurement values, for example, reflection from one surface at three different angles. However, it seems to us that for practical use the most suitable of these may be a reflection and transmission coefficients from the substrate ( $t_-$  and  $r_-$ , respectively), and transmittance and reflection coefficients from the free surface ( $t_+$  and  $r_+$ , respectively):

$$t_- = \frac{E_+ (1 - R_1)(1 - R_2) \exp(2\pi idN/\lambda)}{E \quad 1 - R_1 R_2 \exp(4\pi idN/\lambda)}, \quad r_- = \frac{E_- (1 - R_1)^2 R_2}{E \quad 1 - R_1 R_2 \exp(4\pi idN/\lambda)} + R_1,$$

$$t_+ = \frac{(1 - R_1)(1 - R_2) \exp(2\pi idN/\lambda)}{1 - R_1 R_2 \exp(4\pi idN/\lambda)}, \quad r_+ = \frac{(1 - R_2)^2 R_1}{1 - R_1 R_2 \exp(4\pi idN/\lambda)} + R_2,$$

where  $E$  — the amplitude of the wave incident on the investigated film;  $E_+$  — the amplitude of a wave incident on the film-substrate system;  $E_-$  — amplitude of the wave passing substrate-film system;  $R_1$  — reflectance coefficient at the interface of the film and the substrate under study;  $R_2$  — reflectance coefficient at the opposite edge of the film under study;  $d$  — the thickness of the film;  $\lambda$  — wavelength;  $N$  — complex index of refraction ( $N = n - ik$ ,  $n$  — refractive coefficient,  $k$  — absorption coefficient,  $\varepsilon_1(\omega) = n^2 - k^2$ ,  $\varepsilon_2(\omega) = 2nk$ ).

In is necessary to calculate the square of the corresponding characteristics to calculate the values relating to the intensity.

It should be noted that used earlier formulas derived without consideration of interference, of course, are absolutely incorrect for most wavelengths, and further results of corresponding papers will not be considered [5]. The advantage of such expressions is their simplicity that makes possible the calculations without the use of a computer, but now the computer problem is absent.

The direct task of calculating these three values is not difficult. The situation is different with the inverse task — calculation of optical parameters included in the formulas using the measured values. Particular difficulties is that the accuracy of measurement of these values in the real case is small — less than 5%, it can be estimated slightly higher for transmittance measuring — about 3%.

Despite the high accuracy inherent to optical methods in the measurement of geometric quantities and timing (frequency) characteristics, achieving better results for photometry seems either very difficult (which leads to the growth of these tasks in an independent scientific problem) or even impossible (due to technological limitations in the hardware). Therefore, generally speaking, an attempt to direct joint solution of equations may fail, even though the physical absurdity of this situation is obvious. As stated in [6], even small errors in transmittance or reflection measurements can lead to large errors in the determination of optical constants, which in turn leads to a completely erroneous calculation of the distribution of optical excitation of the thickness. Dependences of the observed values of the thin film optical parameters are very complex, which makes the traditional way to solve this problem unacceptable — Figure 1.

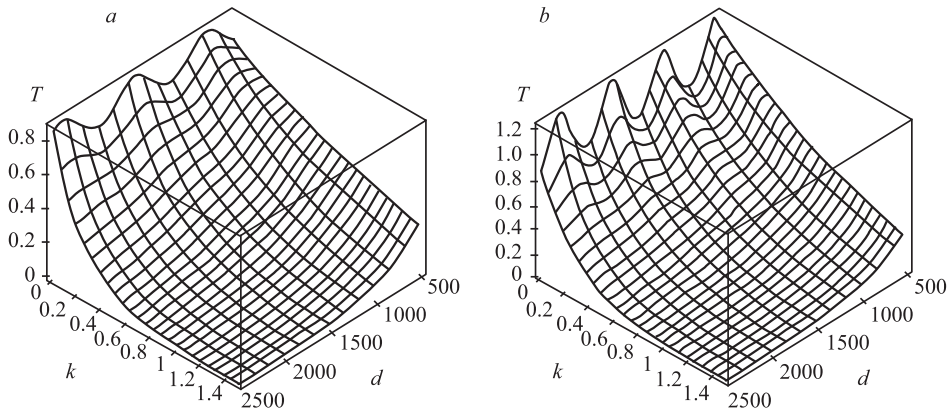


Figure 1. The transmission of a thin absorbing layer as a function of its thickness and absorption coefficient  
 $a - n = 2.5$ ;  $b - n = 3.5$ .

**1. Generalized target model function.** The extended solution understanding in the sense of least squares method was chosen to overcome the above difficulty. In this case a generalized target function is formed [7]:

$$A(n, k, d) = W_1 \left(1 - \frac{R_1}{R_{1t}}\right)^2 + W_2 \left(1 - \frac{R_2}{R_{2t}}\right)^2 + W_3 \left(1 - \frac{T}{T_t}\right)^2, \quad (1)$$

here  $R_{1t}$  — the theoretical value of the reflection of free surface of the film;  $R_{2t}$  — the theoretical value of the reflection of surface adjacent to the substrate;  $T_t$  — transmittance as a function of the unknown quantities  $n$ ,  $k$  and  $d$ ;  $R_1$ ,  $R_2$  and  $T$  — their measured values.

The coefficients  $W_1$ ,  $W_2$  and  $W_3$  in (1) are weighting factors. If the measured values are absolutely accurate and solution of possible a minimum value of  $A$  is 0. However, even in this case, the solution may be non-unique, i. e. the task is not correct according to Hadamard. In the real case of finite measurement errors the purpose of the procedure is to minimize the target function  $A$ .

What is the reason for this choice of the target function form? Three factors should be mentioned that have made this choice the best in our opinion. RMS value is accepted because it allows you to use powerful statistical evaluation  $\chi^2$  criteria such as hypotheses. Inclusion into the target function of the absolute deviations of measured values is not appropriate, as they may vary by one to two orders of magnitude by varying the wavelength of the probe radiation. These values can differ from each other by one order, in which case one of the measured values simply does not affect the result. Whereas the relative error of the measurement of these values lies in the same order. Finally, the weighting factors  $W_i$  allow to take into account different measurement accuracy, respectively, a different effect on the selection of the different values test parameters. These factors were chosen inversely proportional to the relative measurement error. In contrast weighting factors selection when determining the average value their absolute value, of course, does not play any role. In practice, they were chosen to be respectively 0.3, 0.5 and 1.0.

With the proposed method, instead of solving a system of three transcendental equations with three unknowns, the problem was reduced to finding the extremum of a function of three variables. The first numerical experiments show that this function is multiextremal. One of the reasons of multiextremality was the possibility of interference of light beams in thin layers. Standard methods such as steepest descent led to endless loop process at one of the local extrema. Such ambiguity of the solution was repeatedly discussed in the literature on the definition of the optical constants of the layers, and gave rise to the widespread use of one of the methods of the first group (with the use of the Kramers–Kronig relations).

In general, the search for the extremum of multiextremal functions in multidimensional space is an extremely difficult task [8]. Existing strategies of search does not provide any reliable guarantees finding the global extreme. From a practical point of view, proposed in a number of papers the method of step global exhaustive search selection using the Lipschitz condition is absolutely useless. It reduces the main problem to the solution of the auxiliary task of finding the maximum of the derivative in the same multidimensional space. In this case is necessary to carry out the operation of differentiation, which is a problem in itself and may lead to additional errors.

From a theoretical point of view, this case is a classic example of incorrect task, as it has more than one solution. It seems to us that the use of the criterion of minimum complexity of the model in this case is not sufficiently effective as a comparison of functionals

$$\Omega(n, k, d) = \int_{\min}^{\max} \left[ A^2(n, k, d) + A'^2(n, k, d) \right] ds$$

does not provide statistically significant differences for different sets of variables  $\{n, k, d\}$  under the condition of low measurement accuracy, not to mention the mentioned derivative computation difficulties.

**2. Algorithms for determining the parameters of thin film.** In a particular application, we can use a redefinition of the task, if not mathematically, in the physical sense of the word. Indeed, the target function  $A$  is among others dependent on the

wavelength  $\lambda$ , as well as the optical parameters  $n$  and  $k$  of material. In addition to the obvious requirement of the existence of a target function extremum for some values of the variables, it is possible to impose the condition of continuity of optical parameters with respect to wavelength. Since the required variables  $n$ ,  $k$ , and  $d$  are physical quantities, it can be said that in the linear approximation

$$\begin{aligned} n(\lambda + \Delta\lambda) &= n(\lambda) + \frac{dn}{d\lambda}\Delta\lambda, & k(\lambda + \Delta\lambda) &= k(\lambda) + \frac{dk}{d\lambda}\Delta\lambda, \\ d(\lambda + \Delta\lambda) &= d(\lambda) + \frac{dd}{d\lambda}\Delta\lambda = d(\lambda) \end{aligned}$$

(it is obvious that the film thickness does not depend on the measurement conditions). Carrying out measurements at different wavelengths  $\lambda_i$ , we are able to reject solutions which lead to discontinuous functions of  $n$  and  $k$ . An additional criterion for the correctness of the decision may serve the Student's  $t$ -test. Calculating the  $l$  values of  $d$  denote them as  $\{d_i\}$  on all available wavelengths  $l$ . Define the  $m$  values of sample means  $\bar{d}_m$  and variances  $s_m^2$  according to the rule

$$\bar{d}_m = \frac{1}{l-1} \sum_{i \neq m}^l d_i, \quad s_m^2 = \frac{1}{l-2} \sum_{i \neq k}^l (d_i - \bar{d}_m)^2,$$

and, using Student's criterion, we obtain that if for all  $m$

$$\frac{\bar{d}_m - d_m}{s_m} < t_{l-2, 0.95}, \quad (2)$$

then this set of solutions corresponds to a confidence level of 95% of the assumption of the constancy of  $d$ . Sets contradicting this condition should be omitted. This procedure is quite correct [9], but too time-consuming and leads to the calculation of a large number of false choices. Therefore, this procedure has been improved for practical implementation.

In the first stage there is no a priori information (except for general physical considerations, i. e. reduced to physically thinkable restrictions on the values) to estimate all the unknown variables. And all thinkable space of values, i. e. 1.3–4.0 for  $n$ , 0.0–4.0 for  $k$ , and 10–100 nm for  $d$  is divided into intervals in steps of 0.1, 0.05 and 5, respectively. Minimum is searched around each of the initial values by the Fletcher–Reeves method [10], which is a modified method of steepest descent. In this case, the direction of the target function gradient (discrete components 0.1 for  $n$  and the  $k$ , 5 nm to  $d$ ) is determined in each initial point, a few steps done in the direction against the gradient until reaching a minimum value, the gradient is again determined, and the procedure is repeated. If the initial step selected for the calculations led to a cycle, i. e. determining the position of the extremum of target function with an accuracy of the value of this step, the step value is reduced by an order, and the steepest descent procedure is continued again. When the program goes in cycle with step reduced by two orders of magnitude, the program is stopped, and the resulting values of variables are considered relevant to a target function local minimum. The accuracy of calculation is to be about 0.001 for  $n$  and  $k$ , and 0.05 nm for  $d$ , considerably exceeding the accuracy because of measurement errors.

As a result of the first stage the program forms an array of 1000 values of variables  $\{A_{ilm}\}$  meeting the target function minimum obtained for some initial point  $n_i, k_l, d_m$ . If there is only one (global) extremum, these values are identical up to the value of the order of the last step.

The target function is multiextremal, therefore, although many initial values of the variables lead to the same extremum, variable values selection variants yet proved quite

a lot. From these values were rejected those that correspond to the nonglobal extrema, i. e. those in which the target function more than twice obtained for other initial values. Typically, after the rejection there was three to six sets  $\{n_i, k_i, d_i\}$  statistically different from each other.

In the following stage, i. e. at other wavelengths there is no need to investigate the extremum of all physically possible values of the variables. Due to the continuity of the functions  $n(\lambda), k(\lambda)$  and the constancy of  $d$  as the initial sets we selected sets  $\{n_i, k_i, d_i\}$  defined in the first stage. And the steepest descent procedure repeats as described previously. For each of the following wavelength values, the same procedure is repeated. After four or five of such procedures, the first test of Student criterion was performed. If it turns out that (2) is violated, the corresponding chain broke off, and further calculations with given initial values of the parameters were not fulfilled. As a rule, after the calculations for six to eight wavelengths only one solution left.

With this algorithm run time is significantly reduced. Algorithms of programs are shown in Figure 2, I-III.

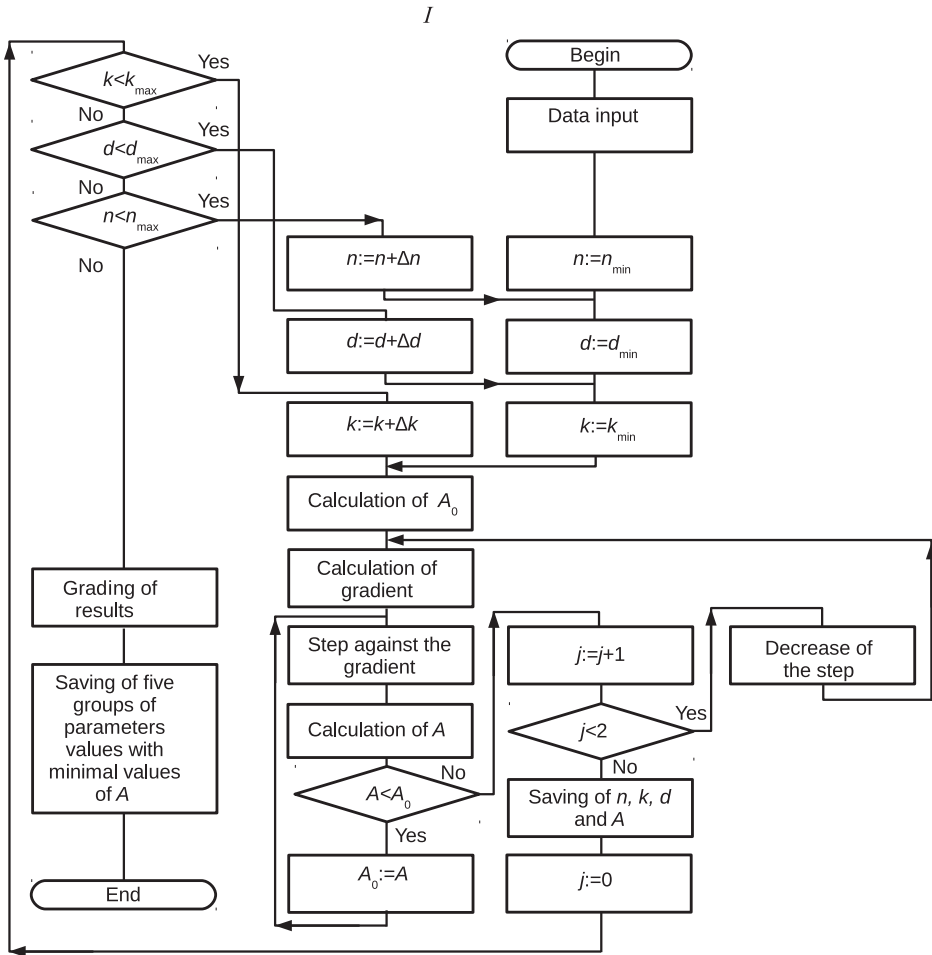
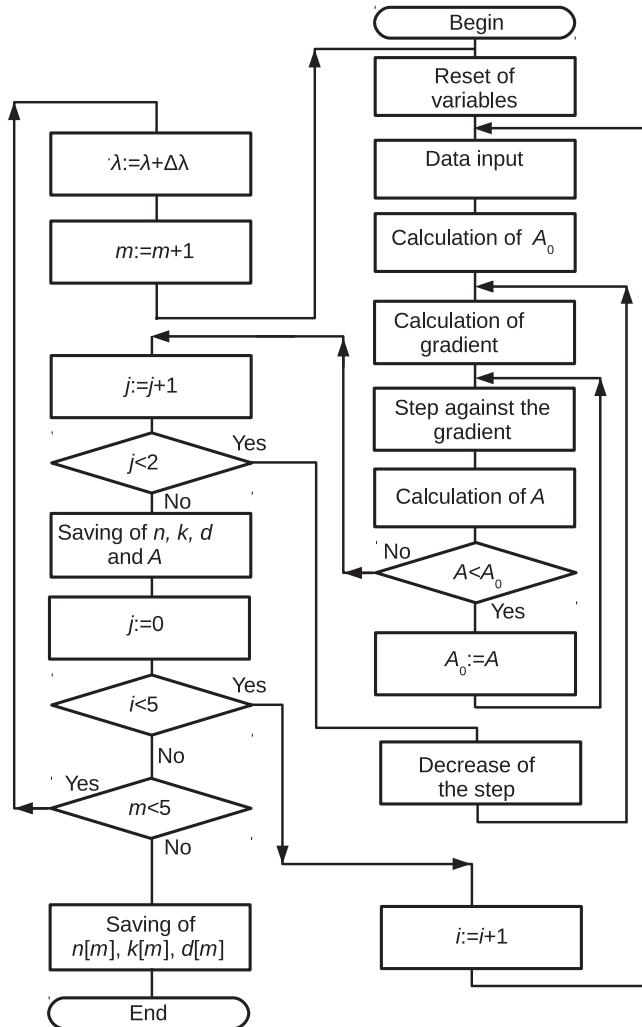


Figure 2. The algorithm of the first (I), second (II) and third (III) stages

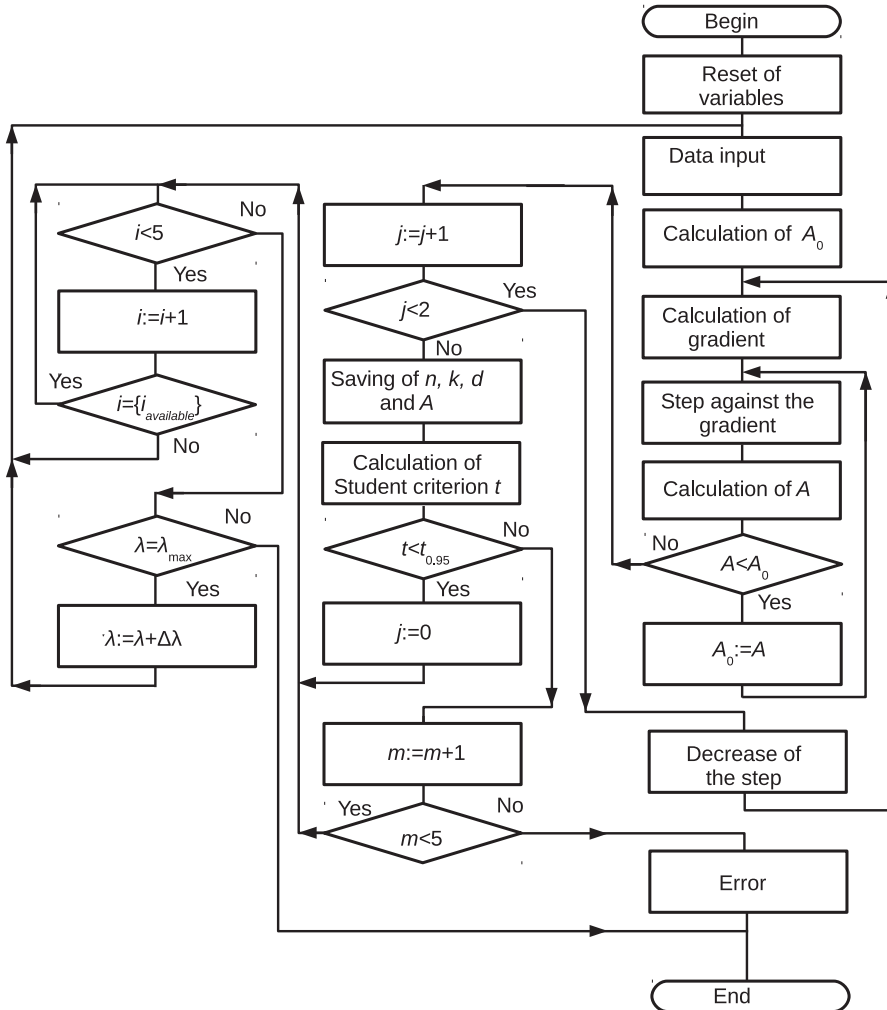
Selection of the wavelength of the initial values is very significant, because the initial value of the wavelength can be selected arbitrarily by researcher.

It is possible that from the standpoint of eliminating random measurement errors, randomized wavelength selection would have been more effective, but we are deprived of the possibility of using the continuity of the functional dependence of the optical parameters of the material on the wavelength. As it turns out, more stable solutions can be obtained

II



of determining the optical parameters of the thin layer



End of Figure 2

at the initial point corresponding to the minimum transmittance that is in the short wavelengths. This is natural, since in this case the interference effects play a much smaller role. For very large values of the absorption coefficient the variation of intensity of the light field becomes almost exponential, and the solution is quite stable.

**Conclusion.** The proposed algorithms were used to calculate the characteristics of the compounds intensively used in the photoelectronic devices, namely multi-alkali photocathode, which is a complex compound having in its composition antimonides of potassium, sodium and cesium. As in other cases, the optical properties play an important role in the functioning of devices, while the differences in the optical constants determined this compound are sufficiently large, even if the determination is made in the same laboratory. This is natural, considering that the process of manufacturing this compound comprises up to 30 operations only on the last stage of the vacuum treatment. Our results are presented in Figures 3, 4. The value of  $n$  varies quite weak but the  $k$  varies rather



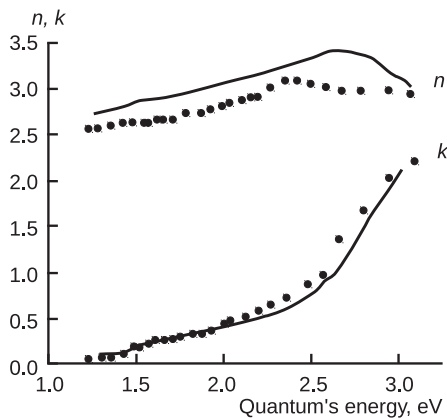


Figure 3. Optical constants of multi-alkali photocathode according to [9] (solid lines) and our experimental results (dots)

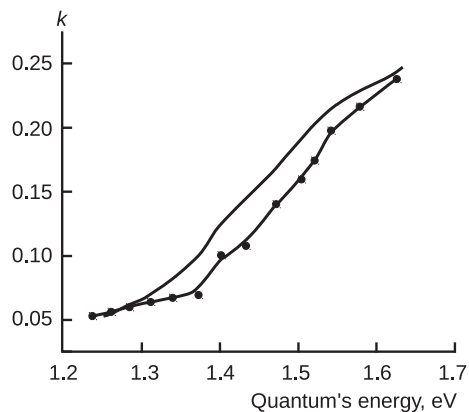


Figure 4. The multi-alkali photocathode absorption index in the near-threshold region of the spectrum according to [9] (solid line) and our experimental results (dots)

sharply as would be expected for the semiconductor material near the intrinsic absorption edge. When compared with the data given in the literature, our sample absorption coefficient is significantly greater. Compared to modern data the value of  $k$  in our samples is noteworthy smaller, especially in the near infrared region of the spectrum. Performed “reverse” calculation (the total absorption of the known optical constants) shows that the samples provided to us have about half the absorption of light, and therefore, may not have as high a sensitivity as described in [11]. Increase in thickness, which also leads to an increase in absorption, it is not sufficiently effective, especially from the standpoint of electrons output in a vacuum, since increased thickness causes an increase in power loss at the stage of transportation.

## References

1. Egorov N. V., Antonova L. I., Antonov S. R. Study of the emission properties of a W-Cs<sub>3</sub>Sb field-emission cathode. *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Technique*, 2007, vol. 1, issue 4, pp. 487–495.
2. Egorov N. V., Karpov A. G., Antonova L. I., Fedorov A. G., Trofimov V. V., Antonov S. R. Technique for investigating the spatial structure of thin films at a nanolevel. *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*, 2011, vol. 5, issue 5, pp. 992–995.
3. Kossel D., Deutscher K., Hirshberg K. Interference photocathodes. *Advances in electronics and electron physics*, 1969, vol. 28a, pp. 419–431.
4. Szozyrlowski J. Determination of optical constants of real thin films. *J. Phys. D. Appl. Phys.*, 1978, vol. 11, pp. 583–594.
5. Sizelove J. R., Love III J. A. Analysis of Translucent and Opaque Photocathodes. *Appl. Optics*, 1967, vol. 6, pp. 356–357.
6. Timan H. Optical characteristics and constants of high efficiency photoemitters. *Revue Technique Thomson CSF*, 1976, vol. 8, pp. 49–80.
7. Karpov A. G., Klemeshev V. A., Trofimov V. V. Matematicheskie osnovy metodov obrabotki informacii dielektricheskoi spektrometrii tonkikh plenok [Mathematical foundations of information processing methods for dielectric spectroscopy of thin films]. *Vestnik of Saint Petersburg State University. Series 10. Applied mathematics. Computer sciences. Control processes*, 2015, issue 4, pp. 13–26. (In Russian)
8. Pshenichny B. P., Danilin Y. M. *Chislennyye metody v ekstremal'nykh zadachakh [Numerical methods in extreme tasks]*. Moscow, Nauka Publ., 1975, 320 p. (In Russian)

9. Tiurin Iu. N., Makarov A. A. *Statisticheskii analiz dannykh na komp'yutere* [*Statistical analysis of the data on the computer*]. Moscow, Infra-M Publ., 1998, 528 p. (In Russian)
10. Dai Y. H., Yuan Y. Convergence properties of the Fletcher–Reeves method. *The IMA Journal of Numerical Analysis*, 1996, vol. 16. pp. 155–164.
11. Kaiser W. J., Bell L. D. Direct investigation of subsurface interface electronic structure by ballistic-electron-emission microscopy. *Phys. Rev. Lett.*, 1988, vol. 60, pp. 1406–1410.

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