# Waveguide Spectroscopy of Thin Films

## A. V. Khomchenko

*Institute of Applied Optics, National Academy of Sciences of Belarus, Mogilev, Belarus*
*e-mail: ipo@physics.belpak.mogilev.by*
Received June 19, 2000; in final form, November 13, 2000

**Abstract**—A waveguide method of measurement of the absorption spectra of thin films in the range of their transparency is considered. The absorption spectra obtained by this method for the thin films of tin oxide and zinc oxide in a wavelength range from 400 to 800 nm are presented. The error of measurement of the absorption spectrum did not exceed 5% for an ~0.1-μm-thick film with an absorption coefficient of ~50 cm$^{-1}$. Possibilities and limitations of the method are discussed. © *2001 MAIK "Nauka/Interperiodica".*

The electrical and optical properties of semiconductor and dielectric thin-film structures are determined to a considerable extent by the characteristics and distribution of electron states in the forbidden band. For polycrystalline and amorphous films prepared under nonequilibrium conditions, the properties of which depend on the features of the deposition process, these data can be obtained only in experiment. Certain information in this respect is provided by the optical spectroscopy measurements in the region of frequencies below the fundamental absorption edge, However, the existing optical methods are difficult to employ for measuring the absorption spectra of thin films with the absorption coefficients $\alpha < 10$ cm$^{-1}$. This is related to the fact that a direct measurement of the absorption for $\alpha d \ll 1$, where $d$ is the film thickness, becomes uncertain. The photoconductivity techniques, which allow the material parameters to be determined for $\alpha \approx 1$ cm$^{-1}$ in semiconductor materials, are poorly applicable to dielectric films. For this reason, a considerable effort by researchers is devoted to the development of better methods for the study of thin films [1].

A high-precision method for the diagnostics of thin films is offered by the waveguide techniques. An advantage of these techniques is a high resolution and the ability of directly determining the refractive index of thin films with thicknesses from a few tenths of a micron to several tens of microns. Attempts at determining the spectral dependence of the absorption coefficient of thin films were undertaken within the framework of the surface electromagnetic wave spectroscopy [2], which allowed the vibrational spectra of monomolecular layers and natural oxide films on the surface of metals to be studied. This method has proved to be rather effective in the IR spectral range. In the visible range, it was suggested to study the spectra of absorbing films using the optical waveguide modes [3]. For this purpose, the sample films were placed on the waveguide surface, so that the radiation intensity attenuation in the waveguide was modified by the absorption in the film

due to the waveguide mode field penetration into the adjacent medium. This method gave satisfactory results for ultrathin films (with a thickness of 10–15 Å). The spectral dependence of the absorption coefficient of thin films was also studied by directly measuring the real $h'$ and imaginary $h''$ parts of the propagation constant $h$ of the waveguide modes in a two-prism geometry [4]. Unfortunately, the need for an additional adjustment of the prismatic coupling device depending on the incident radiation frequency and the dependence of $h''$ on the prism–waveguide coupling efficiency restricts the applicability of this method.

All the above problems can be eliminated to a certain extent using the method of waveguide spectroscopy described below. The proposed approach to measurements of the spectral dependence of the absorption coefficient of thin films is essentially a development of the method used previously [5, 6], representing an extension of these measurements to the case of non-monochromatic radiation. The measurements involve registration of the spatial Fourier spectrum of a light beam reflected from a prismatic coupling device upon a waveguide mode excitation in the thin-film structure studied. An analysis of the experimental results showed that the error of determination of the waveguide mode propagation constant relative to the $h''$ value measured at a laser radiation frequency did not exceed 1%, provided that the spectral bandwidth of the probing radiation was restricted to below 60 nm and an appropriate optical scheme is employed. Evidently, the effect of the degree of coherency on the accuracy of restoration of the waveguide mode parameters requires additional investigation, because the formation of an intensity distribution pattern in the reflected beam cross section is related to the interference of light fields. However, the results of our measurements showed that the proposed method actually allows the spectral dependence of the absorption coefficient of thin films to be determined in a sufficiently broad range of wavelength, the more so that the prismatic element used for the optical
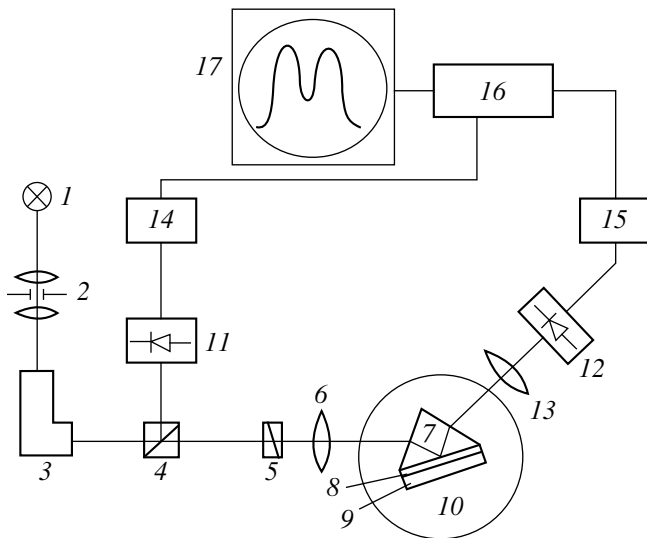
**Fig. 1.** A schematic diagram of the experimental setup: (*1*) frequency-tunable radiation source with controlled intensity; (*2*) collimator; (*3*) monochromator; (*4*) beam splitting cube; (*5*) polarizer; (*6*) focusing device; (*7*) prismatic coupling device; (*8*) thin-film waveguide (sample); (*9*) substrate; (*10*) rotary table; (*11*, *12*) photodetectors; (*13*) optical Fourier converter; (*14*, *15*) intensity-measuring units; (*16*) analog-to-digital converter; (*17*) computer.

waveguide excitation restricts the spectral bandwidth to 10–40 nm [7].

Upon the waveguide mode excitation, the display shows a series of dark *m*-lines. Each line considered separately exhibits a spatial intensity distribution of its own observed in the reflected light [5]. By properly selecting the exciting beam parameters, this pattern can be readily recorded. These measurements were performed in a specially designed computer-controlled setup, a schematic diagram of which is presented in Fig. 1. The setup measures the intensity of a beam reflected (at a fixed incidence angle) from a prismatic coupling device. A confined light beam from a frequency-tunable radiation source is incident onto a prismatic coupling device *7*. This device represents an equilateral measuring prism mounted on a rotary table *10*. The incident light beam excites a waveguide mode in a sample film *8* on substrate *9*. The complex propagation constant *h* of this mode depends on the optical parameters and thickness of the film. The prism was made of an optical glass (TD12 grade) with a refractive index of 1.77905 at a wavelength of 0.6328 μm. The measurements can be performed using various polarizations of the incident light. It was also possible to control the light beam radius from 15 to 150 μm. The transverse beam size was measured for an intensity level of $I = I_0 e^{-1}$, where $I_0$ is the light intensity at the beam axis.

The measured sample on substrate *9* was pressed against the coupling prism surface so as to provide for the optimum conditions of the optical mode excitation. A spatial distribution of the intensity of the reflected light

beam was measured using a photodetector array *12*. The axis of rotation of the detector array coincides with that of the rotary table, while the working detector area is situated in the focal plane of the objective lens *13* transmitting the reflected beam. The incident light intensity was measured with photodetector *11*. The output signal was digitized and transferred via interface to the computer memory. The instrumental error of determination was $2 \times 10^{-5}$ for the optical mode excitation angle and 0.1% for the light intensity.

As the probing radiation frequency is varied during the measurements, the pattern of the intensity distribution exhibits a transformation. Using the gradient descent method (the applicability of which to restoring the mode parameters was justified in [6]), it is possible the determine the real *h'* and imaginary *h''* parts of the complex propagation constant *h* for an asymmetric curve of the reflected beam intensity distribution. The index of refraction, absorption coefficient, and thickness of the sample film can be determined using the *h* values determined for various modes [6]. It should be emphasized that the approach proposed for determining the propagation constant allows the effect of the prismatic coupling device to be taken into account, thus giving the values of parameters independent of the prism–waveguide coupling efficiency. Note that the method does not involve absolute measurements of the light intensity. Use of a wide (in the wavevector space) light beam and application of the gradient descent method for determining *h* eliminates the need for any additional adjustment of the prismatic coupling device depending on the incident radiation frequency. As a result, the measurements reflect a variation of the absorption coefficient of a sample thin film in a preset spectral interval and allow the refractive index *n* and thickness of the sample to be determined. The film thickness determination can be used for verification of the waveguide spectroscopy data by comparing this value to a thickness determined by an independent technique such as the multibeam interference or profilography.

In this experiment, the measurements were performed for a series of thin films prepared by the RF sputtering of a ZnO ceramic target onto a quartz glass substrate at $T = 300$ K. The film had a thickness of 1.5 μm and could transmit five waveguide modes. Figure 2 shows the results of measurements of the $h''(\lambda)$ spectrum using a third-order waveguide mode with TE polarization. The same figure shows the plots of $n(\lambda)$ and $k(\lambda)$ values determined from the waveguide measurements, where *k* is related to the absorption coefficient by the relationship $\alpha = 4\pi k/\lambda$. The average sample film thickness is $d = 1.50 \pm 0.01$ μm; the film thickness determined on a profilometer was $1.50 \pm 0.02$ μm. As seen from the curves in Fig. 2, the spectral dependence of the absorption coefficient of the films studied is well described by the $h''(\lambda)$ curve. This result indicates that the measurement of the $h''(\lambda)$ value is sufficient for

determining the absorption coefficient of the film material.

Analogous measurements were also performed for the films of $SnO_2$:$Sb_2O_5$, $SnO_2$:$Al_2O_3$, and $SnO_2$:$WO_3$ deposited by the same method onto quartz glass substrates at 420 K. The $SnO_2$:$Sb_2O_5$ film had a thickness of 0.7 μm and could transmit two TE-polarized waveguide modes. Figure 3 shows the $h''(\lambda)$ curves for the $SnO_2$:$Sb_2O_5$ films doped with antimony to various degrees as well as the curves for $SnO_2$:$Al_2O_3$ and $SnO_2$:$WO_3$ (measured using the TE-polarized fundamental mode). As seen from these spectral data, a modification of the film composition is manifested by changes in the structure and positions of the absorption bands in the spectral range of transparency.

A sensitivity of the proposed method can be demonstrated by the following experimental results. As is known, the films of tin dioxide are widely used in the active elements of gas sensors [8]. The electrical properties of these films significantly change already upon adsorption of a single monolayer of gas molecules. It was natural to expect that the spectral parameters of such films would exhibit adsorption-induced changes as well. Figure 3 shows the spectral dependence $h''(\lambda)$ for a $SnO_2$:$Sb_2O_5$ film measured in pure air and in a mixture of air with ammonia vapors (curves 5 and 6, respectively). As seen, the presence of ammonia at a concentration of 0.01 mg/l produces a noticeable change in the film parameters, which is revealed by the absorption spectrum measured.

A total relative error of the determination of $k(\lambda)$ with an allowance for the systematic uncertainty did not exceed 0.03. The spectral interval of measurements was limited by the available equipment. Realization of the waveguide spectroscopy method encounters problems in determining the $k(\lambda)$ values below $10^{-5}$, which is explained by restrictions of the waveguide measurements related to a "leak" of the waveguide mode energy in the prismatic coupling device [6]. This circumstance should be taken into account during the measurements of parameters of weakly absorbing films: the method is applicable to the films with thicknesses below 1 μm, provided that the absorption coefficient is ~ 1 cm⁻¹ ($k =$ $2 \times 10^{-6}$). For sufficiently thick semiconductor films ($d \sim 1$ μm), the experimental procedure is simplified because $k \approx h''$ [9] and it is sufficient to measure only $h''$ in order to determine the absorption coefficient of the film material.

The condition that guided modes must exist in the structure studied is not necessary, provided that the film is applied onto a weakly absorbing substrate (i.e., when the absorption coefficient of the substrate is significantly smaller than the $k$ value of the film studied). In this case, the refractive index of the substrate can be even greater than that of the film. The film parameters can be determined from data on the propagation constant of the outgoing modes [6].
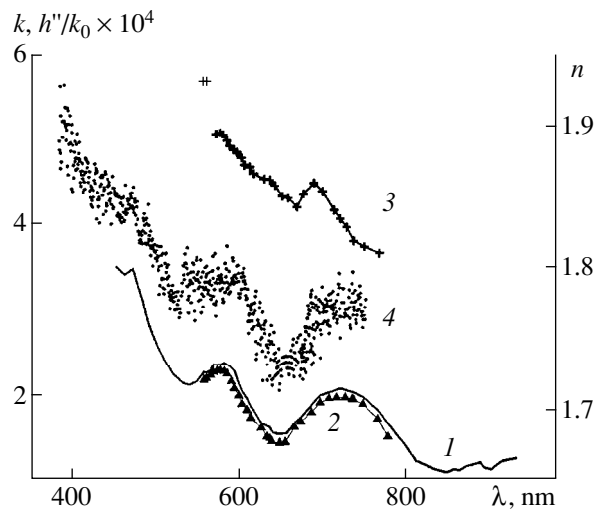


**Fig. 2.** Waveguide spectra of (1) $h''$, absorption coefficient $k(\lambda)$ (2), and (3) refractive index $n(\lambda)$ of a ZnO film. Curve 4 shows a $k(\lambda)$ curve measured by the transmission spectroscopy method.
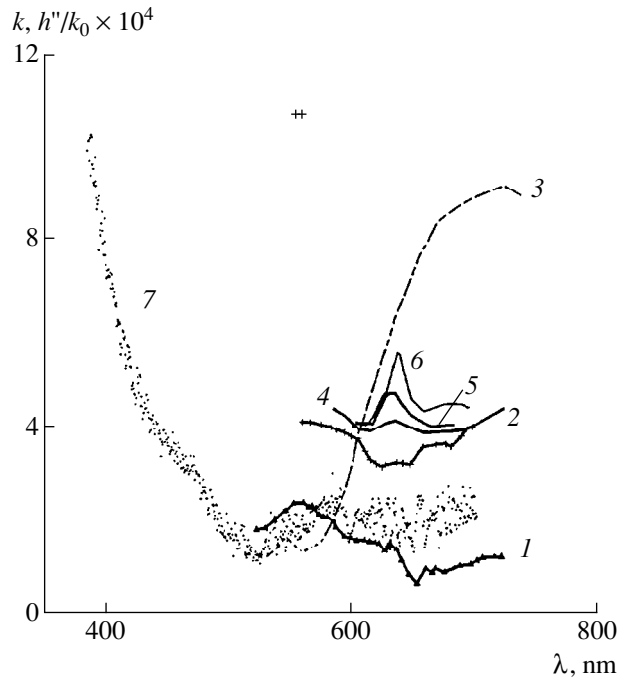


**Fig. 3.** Waveguide spectra of $SnO_2$ films with various dopants: (1, 4, 5) $SnO_2$:$Sb_2O_5$ (with various Sb concentrations, $C_1 < C_2 < C_3$, respectively); (2) $SnO_2$:$Al_2O_3$, and (3) $SnO_2$:$WO_3$. Spectra 5 and 6 were measured for the same $SnO_2$:$Sb_2O_5$ sample in pure air and in air with ammonia vapors, respectively. Curve 7 shows a $h''(\lambda)$ curve for $SnO_2$:$WO_3$ measured by the transmission spectroscopy method.

For the comparison, the spectral dependence of the absorption coefficient of thin films was also measured by the transmission spectroscopy. Figure 2 (curve 4) shows the corresponding spectrum of $k(\lambda)$ for a zinc oxide film; Fig. 3 (curve 7) shows the optical transmis-

sion data for a $SnO_2:WO_3$ film. As seen, the shapes of the spectra obtained by the two methods exhibit good correlation. A maximum discrepancy between $k(\lambda)$ and $h''(\lambda)$ cures was observed for thin films in the long-wavelength spectral region (Fig. 3). This can be explained from the standpoint of the waveguide mode theory [9]. Indeed, an increase in the radiation wavelength leads to a decrease in the effective film thickness; however, the $SnO_2:WO_3$ film thickness was only 0.3 μm and the $h''(\lambda)$ value was not equal to $k(\lambda)$.

The results presented above indicate that the method of waveguide spectroscopy can be used for determining the spectral parameters and optical properties of thin films in the range of their transparency.

## REFERENCES

1. M. A. Bukhshtab, *Measurements of Small Optical Losses* (Énergoatomizdat, Leningrad, 1988).

2. P. I. Nikitin, Sens. Sist. **12** (1), 69 (1998).

3. V. A. Yakovlev, V. A. Sychugov, and A. V. Tishchenko, Pis'ma Zh. Tekh. Fiz. **8** (11), 665 (1982) [Sov. Tech. Phys. Lett. **8**, 289 (1982)].

4. M. Oliver, J.-C. Peuzin, and J.-S. Danel, Appl. Phys. Lett. **38** (2), 79 (1981).

5. V. P. Red'ko, A. A. Romanenko, A. B. Sotskiĭ, and A. V. Khomchenko, Pis'ma Zh. Tekh. Fiz. **18** (3), 14 (1992) [Sov. Tech. Phys. Lett. **18**, 100 (1992)].

6. A. B. Sotskiĭ, A. A. Romanenko, A. V. Khomchenko, and I. U. Primak, Radiotekh. Élektron. (Moscow) **44** (5), 1 (1999).

7. S. B. Mendes, L. Li, J. J. Burke, *et al.*, Appl. Opt. **34** (27), 6180 (1995).

8. V. V. Kisin, V. V. Sysoev, and S. A. Voroshilov, Pis'ma Zh. Tekh. Fiz. **25** (16), 54 (1999) [Tech. Phys. Lett. **25**, 657 (1999)].

9. A. M. Goncharenko and V. A. Karpenko, *Foundations of the Theory of Optical Waveguides* (Nauka i Tekhnika, Minsk, 1983).

*Translated by P. Pozdeev*