Optica Applicata, Vol. XVI, No. 2, 1986

Modification method of wavelength modulation spectroscopy *

Z. GUMIENNY, J. MISIEWICZ

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-372 Wrocław, Poland.

A measuring set-up has been made to determine spectral dependences of optical coefficients and the derivative of those dependences by use of the wavelength modulation method. To this end a high resolution spectrometer was equipped with a vibrating plane-parallel plate with suitable electronic and mechanic systems. This set-up has been used in measurements of absorption near fundamental edges of Si and Zn_3P_2, the resolution of which was better than ± 0.002 eV.

1. Introduction

The development of the studies on the fine optical transitions in semiconductors requires a continuous improvement of the measuring techniques. The relative measurements are more and more frequently replaced by the absolute measurements, while the static methods are supplemented with the modulation methods. A common feature of all the modulating methods is the fact that the object of the measurements is the derivative of the response (for instance, transmission or reflection) with respect to the chosen parameter. High accuracy of such measurements may be achieved by applying phase-sensitive detectors.

All the modulation methods may be divided, according to the choice of the differentiating variable, into two groups [1]: (i) the methods of wavelength modulation, in which the wavelength is the differentiating variable, and (ii) the methods of external condition modulation, in which external perturbation, such as mechanical deformation, temperature, electric and/or magnetic field, applied to the sample, is differentiating variable.

The measuring system described in this paper is based on the technique of wavelength modulation. This method does not destroy the sample state and its technical realization is relatively simple. The results obtained by this method make it possible to increase considerably the accuracy of semiconductor band-structure investigations.

---

* This work has been carried on under the Research Project of IF PAN.

2. Measuring set-up

The set-up based on the GDM–1000 Zeiss monochromator consists of two independent optical and electronic parts, both being schematically shown in Figs. 1 and 2, respectively.

2.1. Optical part

The optical part of the system used was extensively described previously [2]. The Zeiss GDM–1000 grid monochromator has been equipped with the amplitude modulator AM of frequency ω, and the wavelength modulator WM of frequency Ω. A plane-parallel vibrating plate used as the WM was made of fused quartz, without any strains. The use of prisms (in the term of complete internal reflection) instead of mirrors allows us to avoid difficulties occuring when the anisotropic crystal is measured, e.g., under linearly-polarized light. The light beam presented in Fig. 1 is intended for reflectivity measurements, but a simple change (PM will measure light density transmitted by specimen instead of the density of reference beam, as in Fig. 1) makes possible the transmittance measurements.

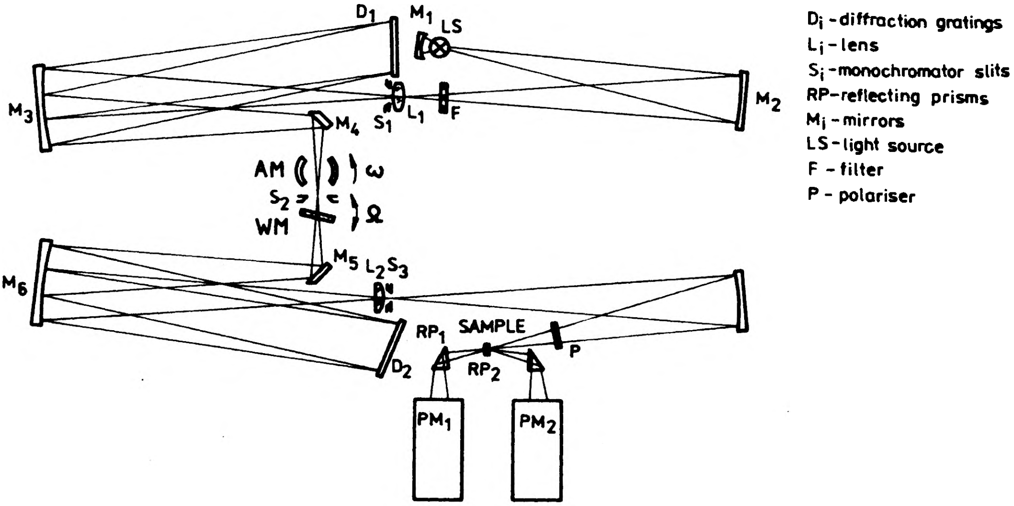

Fig. 1. Scheme of the optical part of the described set-up (details see in the text)

2.2. Electronic part

The electronic part of the set-up consists of several simple elements presented in Fig. 2. The photoresponse H_1 of the PM_1 photomultiplier is a reference signal for reflectivity measurements and the measuring signal for transmittivity measurements, and contains two parts of frequencies ω and Ω, respectively, for transmittivity measurements given by:

$$H_1'(\omega) = I S_1 T, \tag{1a}$$

$$H_1''(\Omega) = k I S_1 T + I S_1 \frac{dT}{d\lambda} + I T \frac{dS_1}{d\lambda} + T S_1 \frac{dI}{d\lambda}. \tag{1b}$$

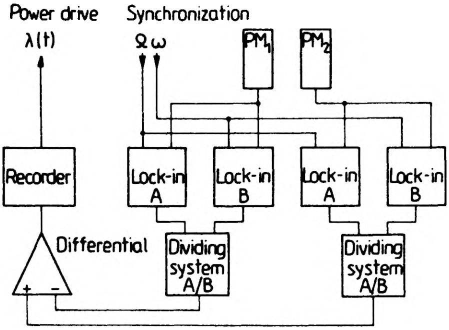

Fig. 2. Electronic block scheme of the presented set-up (details are described in the text)

The photoresponses of the PM$_2$ photomultiplier H_2 are inversely related to the signals of PM$_1$ (as reference and measuring signals) and are as follows:

$$H_2'(\omega) = I S_2, \tag{2a}$$

$$H_2''(\Omega) = k I S_2 + I \frac{dS_2}{d\lambda} + S_2 \frac{dI}{d\lambda} \tag{2b}$$

where I is a photon-flux density irradiating the specimen measured, T is a specimen transmittance, and S_1 and S_2 are the spectral sensitivities of photomultipliers. The first terms in Eqs. (1b) and (2b) are due to the amplitude modulation given by element WM (see above) and have a double frequency, 2Ω, fortunately, tuned well (k-time) by homodyne nanovoltmeters.

Next, they practically vanish due to electronic data handling. We can get the final signal by the use of the dividing element which allows us to obtain the ratios of H_1''/H_1' and H_2''/H_2' and if the multipliers are identical (i.e. they have the same spectral characteristics) to record the final signal

$$\frac{H_2''}{H_2'} - \frac{H_1''}{H_1'} = -\frac{dT}{dT\lambda}. \tag{3}$$

When the reflectivity measurements are performed, coefficient R replaces the transmittance T in Eqs. (1) and (2), and we get

$$\frac{H_1''}{H_1'} - \frac{H_2''}{H_2'} = \frac{dR}{R d\lambda}. \tag{4}$$

3. Transmittance and absorption correlation

Absorption spectrum $\alpha(\lambda)$ gives important information about the energy-band structure of semiconductors, especially in the parts in which the absorption coefficient rises sharply (or its derivative has a maximum) as, e.g., in the region of fundamental absorption edge. Therefore, the correlation between transmittance and its derivative (measured usually) and absorption spectrum (needed for the above mentioned reason) is of great importance.

Transmittance of light passing normally through a plane-parallel sample, interference effects being neglected, is given by the well-known formula

$$T=\frac{(1-R)^2\exp(-\alpha t)}{1-R^2\exp(-2\alpha t)} \tag{5}$$

where t is the specimen thickness, and R and α are its reflectivity and absorption coefficients, respectively. From Eq. (5) we easily get

$$\frac{dT}{d\lambda}=\frac{2(1-R)\exp(-\alpha t)[1+R(1-2R)\exp(-2\alpha t)]}{[1-R^2\exp(-2\alpha t)]^2}\frac{\partial R}{\partial\lambda} -\frac{t(1-R)^2\exp(-\alpha t)[1+R^2\exp(-2\alpha t)]}{[1-R^2\exp(-2\alpha t)]^2}\frac{\partial\alpha}{\partial\lambda}. \tag{6}$$

The first term in Eq. (6) may be neglected in that (narrow) spectral region in which R is a very slowly-varying function of wavelength λ, even around the singular points of $R(\lambda)$ plots. Then, we have

$$\frac{dT}{Td\lambda}=-t\frac{1+R^2\exp(-2\alpha t)}{1-R^2\exp(-2\alpha t)}\frac{d\alpha}{d\lambda}. \tag{7}$$

Now, if we take into account the values of R, α, and t, typical of semiconductor specimens ($R = 0.3$, $\alpha t \geqslant 1.4$), we get

$$\frac{d\alpha}{d\lambda}=-\frac{1}{t}\frac{dT}{Td\lambda}, \tag{8}$$

with the error smaller than $1^0/_0$. This means that the transmittance derivative, easily automatic set-up (see above), indicates the singular points and fine structure of $\alpha(\lambda)$ plots with negligible error.

4. Transmittance measurements

Analysis of absorption spectra is one of the most powerful tools in study of the energy-band structure of semiconductors, below and near the fundamental absorption edge (related to the energy gap, and, for example, impurity levels). In spite of the fundamental edge rising sharply, especially for direct band-to-band electron transitions are often observed small changes of $\alpha(\lambda)$ slop, associated with the other electron transitions induced optically. Modulation techniques allow us to resolve many detailes of $\alpha(\lambda)$ plots.

In this way, we have previously investigated the Zn_3As_2 fundamental transmittivity edge (i.e., energy gap) and its temperature dependence [3, 4]. In the middle part of the Zn_3P_2 absorption edge [5] we found a fine structure between the low and high absorption values, part of which, for both light polarizations are presented (as a solid line) in Fig. 3. Applying the method described above, it was possible to estimate accurately the energy position on the maximal slope of the above part of $\alpha(\lambda)$ spectrum (see dashed lines in Fig. 3). This energy, for both the light polarizations, is at 80 K equal to 1.509 ± 0.002 eV [6].

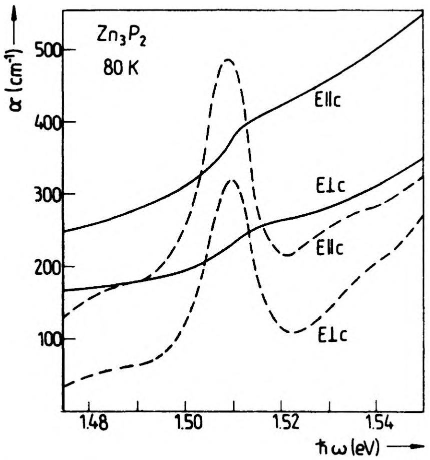

Fig. 3. Plots of absorption and its derivative for Zn_3P_2 in impurity-conduction band transition region

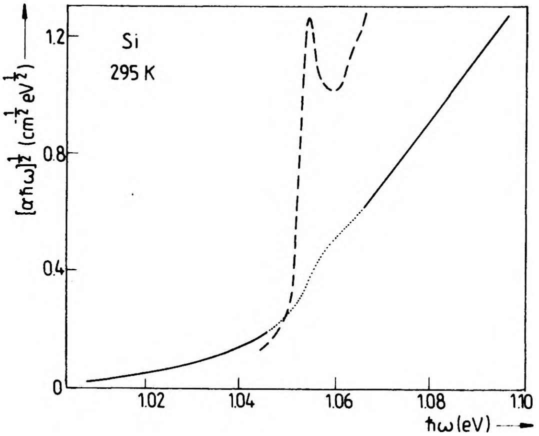

Fig. 4. Plot of absorption and its derivative for Si in the phonon-exciton transition region

The observed threshold is probably connected with impurity level-conduction band transitions [7].

As the examples of the resolution which may be obtained in this set-up are the plots of absorption and its derivative for silicon, presented in Fig. 4. The energy observed at phonon-exciton peak is equal to 1.0547 ± 0.0003 eV and is the same as that stated in paper [8].

References

[1] CARDONA M., *Modulation Spectroscopy*, Academic Press, New York 1969.
[2] GUMIENNY Z., MISIEWICZ J., Optica Applicata **12** (1982), 37.
[3] MISIEWICZ J., PAWLIKOWSKI J. M., Solid St. Commun. **32** (1979), 687.
[4] BECLA P., GUMIENNY Z., MISIEWICZ J., Optica Applicata **9** (1979), 143.
[5] MISIEWICZ J., GAJ J. A., Phys. Status Sol. b **105** (1981), K23.
[6] GUMIENNY Z., Doctor's Thesis, Institute of Physics, Technical University of Wrocław, Wrocław 1982.

[7] Misiewicz J., Sujak-Cyrul B., Szatkowski J., Sierański K., Królicki F., Acta Phys. Polon. **A67** (1985), 125.

[8] Macfarlane G. G., Mc-Lean T. P., Quarrington J. R., Roberts V., Phys. Rev **111** (1958), 125.

Received January 13, 1986
in revised form February 24, 1986

Модификация метода модуляции длины волны

Изготовлен стенд для спектральных измерений зависимости оптических коэффициентов, а также производных этих зависимостей методом модуляции длины волны. Для этого был использован монохроматор большого разрешения с вибрационной плоскопараллельной пластинкой вместе с соответствующей электрической и механической системой. Этот стенд был использован для измерений абсорбции Si и Zn_3P_2 вблизи основного края абсорбции с разрешением лучшим, чем 0,002 eV.