Belarusian State University

Department of Energy Physics

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Guidelines for laboratory work

Study of semiconductors by UV-Vis spectroscopy

The purpose of work is to study the theoretical basics and practical implementation of determination of the semiconductor materials’ parameters by transmission and photocurrent spectroscopy.

Theoretical basics

Light absorption in semiconductors. Fundamental absorption. There are different mechanisms of light absorption by semiconductors: interband (fundamental) absorption, dopant absorption, excitonic absorption, absorption by free charge carriers, absorption by crystalline lattice. The fundamental absorption, which leads to the generation of electron-hole pairs as a result of optical excitation of electrons from the valence band to the conduction band, will be considered in this lab.

The processes of light absorption must obey the of energy and momentum conservation laws. This, in particular, leads to the fact that the minimum quantum energy sufficient to electron excitation from the valence band to the conduction band is equal to the band gap of the semiconductor. Thus, the red edge of the fundamental absorption allows to determine the most important parameter of semiconductor material – its band gap energy \( E_g \). When \( E_g = 2 \text{ eV} \), the corresponding wavelength is 620 nm, therefore fundamental absorption usually occurs in the visible and near ultraviolet spectral range. That is why the methods of optical spectroscopy related with the fundamental absorption in semiconductors are often called in English literature UV-Vis spectroscopy.

Analyze the momentum conservation law with respect to the fundamental absorption. First of all, let’s note that the wavelength of visible light is by about three orders of magnitude larger than the lattice parameter. Accordingly, the photon wave vector is by three orders of magnitude smaller than the size of the first Brillouin zone. Therefore, with high accuracy we may assume that absorption of a photon of visible light does not change the momentum of the electron. It is known that all semiconductors can be divided into direct band gap and indirect band gap. In the first case, the position of the valence band top and the conduction band bottom coincide in the \( k \)-space (space of wave vectors), in the second case – no (Fig. 1). It is obvious that near the edge of fundamental absorption in the case of direct-gap semiconductors only photon absorption is necessary for the electron transition from V-band to C-band. On the contrary, in the case of an indirect semiconductor, the participation of additional particle, which would change the momentum of the electron, is necessary. As such particle a phonon (quant of the crystal lattice oscillations) acts. It is well known that the probability of the process decreases with increasing the number of particles participating in it. Therefore, light absorption in indirect semiconductors near the absorption edge occurs less intense compared to direct-gap semiconductors.

Remark 1. This fact is of great practical importance, in particular, in solar cell technology. If indirect band gap semiconductors (e.g., silicon) are used for manufacturing of solar cells, it is necessary to use thick (of a few hundred micrometers) layers to absorb sunlight effectively. This leads to an increase in material consumption, as well as increased requirements for quality of the material (as in the case of optical carrier generation away from the p-n-junction in a highly-defective semiconductor recombination losses will be large). On the other hand, in the case of direct band gap semiconductors (CdTe or CIGSS, as example) it is enough to use absorber layers with a thickness of a few micrometers, and the material quality can be relatively low. It is for this
reason that the lowest cost generated photovoltaic energy is achieved to date by using thin film solar cells based on direct band gap materials (CdTe, First Solar company, USA).

From the above discussion, we can conclude that the band gap of a semiconductor can be determined using the relation

$$E_g = \frac{hc}{\lambda_{\text{red}}}$$

where $h$ is the Planck's constant, $c$ – speed of light, $\lambda_{\text{red}}$ – red edge of absorption, i.e. the wavelength from which light absorption occurs. Really, the relation (1) can be used only for a rough estimation of $E_g$. The matter is that in real semiconductors the energy distribution of electronic states differs from the density of states of an ideal crystal shown in Fig. 2a. The reason for this difference is the presence in real semiconductors of inhomogeneities (defects) that create additional (with respect to the periodic field of the lattice) field, the potential of which depends randomly on the coordinates. The presence of such field leads to the appearance of so-called tails of the density of electronic states (Fig. 2b), resulting in the red shift of absorption edge of a disordered semiconductor compared to the ideal crystal.

For the correct determination of the band gap energy one come most often from the fact that the spectral dependence of the absorption coefficient for transitions between the allowed bands is described by relations

$$\alpha = A \left(\frac{hv - E_g}{hv}\right)^{1/2}$$

and

$$\alpha = B \left(\frac{hv - E_g}{hv}\right)^2$$

for the direct and indirect transitions, respectively. In equations (2) and (3) $A$ and $B$ are constants independent of wavelength. It follows from (2) and (3) that the spectral dependences of absorption coefficient must linearize in so-called Tauc coordinates $(\alpha hv)^2$ – $hv$ or $(\alpha hv)^{0.5} – hv$ for direct and indirect transitions, respectively. It is obvious that point of intersection with the abscissa axis determines the $E_g$ value of semiconductor.
In the spectral region corresponding to transitions involving the tails of the electronic density of states, the spectral dependence of the absorption coefficient $\alpha$ is described by the Urbach equation

$$\alpha = \alpha_0 \exp \left( \frac{h\nu - E_U}{E_U} \right),$$

where $\alpha_0$ is a constant, $E_U$ is the Urbach energy that reflects structural disorder and defectsness of a semiconductor. For semiconductors with a high degree of structural perfection the Urbach energy takes values of $10 – 20$ meV, whereas for disordered materials it may be by an order of magnitude larger. It follows from (2) that the slope of $\ln(\alpha) – h\nu$ dependence is reciprocal to the Urbach energy. Thus, the analysis of the optical absorption in the spectral range corresponding to the tails of the density of states allows to determine the Urbach energy and thereby characterize the degree of material imperfection.

**Experimental determination of absorption coefficient.** Typically, when the optical properties are studied, the transmission spectra of the sample $T(\lambda)$ are measured:

$$T(\lambda) = \frac{I(\lambda)}{I_o(\lambda)},$$

where $I_0(\lambda)$ is the intensity of light illuminating the sample, $I(\lambda)$ is the intensity of the light transmitted through the sample. Often one use the term *absorbance* (or *optical density*), which is defined according to the formula (6):

$$Abs(\lambda) = \log \left( \frac{I_o(\lambda)}{I(\lambda)} \right) = -\log(T(\lambda)).$$

The transmission spectrum is connected with the optical absorption coefficient spectrum $\alpha(\lambda)$ and the optical reflection coefficient $R$ as:
\[ T(\lambda) = \frac{(1 - R)^2 \cdot \exp(-\alpha(\lambda) \cdot l)}{1 - R^2 \cdot \exp(-2 \cdot \alpha(\lambda) \cdot l)}, \]  

(7)

where we neglect the spectral dependence of the reflection coefficient.

The optical reflection coefficient \( R \) can be determined from the value of a transmission for the transparency region when \( \alpha(\lambda)=0 \). It is expressed by the formula

\[ R = \frac{1 - T(\lambda)}{1 + T(\lambda)}. \]  

(8)

According to (7), spectral dependence of absorption coefficient of the sample can be computed from the transmission spectra according to the formula

\[
\alpha(\lambda) = -\ln \left( \frac{-(1 - R)^2 + \left( (1 - R)^4 + 4R^2(T(\lambda))^2 \right)^{1/2}}{2R^2T(\lambda)} \right) \cdot l^{-1}, \]

(9)

where \( l \) is a sample thickness. This procedure is applied for semiconductors for the measurements of the optical absorption spectra both in the band to band absorption region as well as in the free carrier absorption region.

**Measurement of the spectral dependence of the photocurrent (photovoltage).** In some cases, the measurement of the transmission spectra of the object it is impossible (for example, if the sample is situated on an absorbing substrate). In this case, to determine the \( E_c, E_U \) parameters, as well as to obtain other important information about the semiconductor, one can use the spectral dependence of the photocurrent (photovoltage) generated by a barrier structure based on it. Let us consider this in more detail.

Let there are a semiconductor (for definiteness, of n-type) and a metal; at that a work function of a semiconductor \( A_s \) is less than the work function of the metal \( A_m \) (Fig. 3a). In accordance with the general principles of thermodynamics, when these materials are joining into a single system, electrons will move from the semiconductor to the metal. A region depleted by free charge carriers (often called as depleted region or space charge region) appears near the surface of semiconductor. The depleted region contains a positive space charge formed by ionized donors. The near-surface region of the metal, in turn, will be enriched with electrons, however, due to the high concentration of electrons in the metal the thickness of this region is very small (1-2 nm). The charges arising in the semiconductor and the metal will lead to an appearance of an electric field (called a built-in) on the boundary between materials and this field will obviously prevent the transfer of electrons from the semiconductor to the metal. Therefore, the equilibrium will be established when the electron transfer due to the difference in the work functions will be compensated by the action of the arising built-in electric field.

Potential difference \( U_0 \) corresponding to the built-in field is called a contact, and

\[ eU_0 = A_m - A_s, \]  

(9)

The appearance of the depleted region in the semiconductor corresponds to the energy band bending upward, as it is known that

\[ n = N_c \exp \left( -\frac{E_C - E_F}{kT} \right), \]  

(10)
where \( n \) is the concentration of free electrons, \( N_c \) – effective density of electronic states in C-band, \( k \) – the Boltzmann constant, and \( T \) – the temperature. Emerged band bending can be viewed as a potential barrier to the transfer of charge from one material to another.

![Diagrams](image)

**Fig. 3** – Contact between semiconductor and metal: (a) – before, (b) – after joining

Integrating twice the Poisson equation over the depleted region, one can obtain

\[
U_0 = \frac{e N_d}{2 \varepsilon_0 \varepsilon} W^2, \tag{11}
\]

where \( e \) is the electron charge, \( N_d \) is the donor concentration, \( \varepsilon_0 \) is the electric constant, \( \varepsilon \) is the permittivity of semiconductor, and \( W \) is the width of SCR. One can draw an important conclusion from (11): the width of SCR is growing when the dopant concentration decreases.

If we apply an external voltage to the considered structure and the electric field corresponding to this voltage is codirectional with the built-in field of the depletion region, it will lead to increase of a barrier at the contact to a value of \( e(U_0 + U) \). Voltage of such polarity is called reverse. The width of SCR will be then determined by relation

\[
U_0 + U = \frac{e N_d}{2 \varepsilon_0 \varepsilon} W^2. \tag{11a}
\]

When the polarity of an external voltage is such that the corresponding to its electric field has opposite directions with respect to the built-in one, the external voltage will reduce the height of the barrier to a value of \( e(U_0 - U) \). Such voltage is called forward. The width of SCR will be determined in this case by relation

\[
U_0 - U = \frac{e N_d}{2 \varepsilon_0 \varepsilon} W^2. \tag{11b}
\]

Similarly, the region depleted by free carriers may result as a result of formation of the contact between a semiconductor and an electrolyte (Fig. 4), as well as on p-n-junction (Fig. 5a) or heterojunction (Fig. 5b).
$E_c$ – bottom of conduction band; $E_v$ – valence band top; $E_F$ – Fermi level; $E_{\text{Ox/Red}}$ – redox-potential of electrolyte particles; $E_{fb}$ – flat-band potential; $\varphi$ – electrochemical potential

Fig. 4 – Scheme of the depletion layer formation in the n-type semiconductor (top) and a p-type (bottom) by immersion into an electrolyte
If a semiconductor containing space charge region is illuminated by the light of the fundamental absorption region, the electric field of SCR will act on the electrons and holes in opposite directions (Fig. 6). This gives rise to appearance between the front (illuminated) and the back sample sides of some potential difference, which is called the barrier photovoltage. When the opposite surfaces are closed to a low resistance load, the current (called photocurrent) in the external circuit will flow. This effect is called the photovoltaic, it lies in the basis of the solar cells.

In the formation of photovoltage (photocurrent) not only carriers generated within SCR participate. If an electron-hole pair appeared in the p-type layer (Fig. 6), there is a probability that the photoelectron will reach the edge of SCR and will be transferred by the electric field to the n-type layer before it recombines with a hole. Similarly, there is a probability that photohole generated in the n-type will reach the edge of SCR and will be transferred by the electric field to the p-type region before it recombines with an electron. To increase the collection efficiency of carriers generated outside the SCR, it is necessary that their life time (diffusion length) have as large as possible values.

Fig. 5 – Formation of depletion region in p-n-junction (on the top) and heterojunction (on the bottom); (a) – before, (b) – after joining

Fig. 6 – Separation of photogenerated charge carriers by the electric field of p-n-junction, leading to photocurrent appearance
Remark 2. There are other possible reasons of the photocurrent (photovoltage) appearance in semiconductors:

1. Ambipolar diffusion of electron-hole pairs from the generation region (thin surface layer) into the bulk. More mobile charge carriers (electrons) are ahead of holes that leads to formation between the surface and the bulk of crystal of potential difference, which is called the Dember photovoltage. This photovoltage is not related to the presence of SCR, it is formed at a distance of the order of the diffusion length from the surface.

2. Recharge of surface electronic states (SES) as a result of lighting leading to the appearance of the photovoltage. When a semiconductor is illuminated by quanta with an energy insufficient for the band-to-band transition, but sufficient for "band – surface level" the transition, the carriers will be excited to these surface levels. Carriers of one sign formed as result of such transitions are free, while the carriers of opposite sign are localized on the surface centers.

Free carriers diffuse into the crystal and between them and the carriers of opposite sign localized on the surface some electric field $E_{SS}$ arises. Photovoltage $U_{SS}$ observed in the experiment corresponds to this field. When the wavelength decreases so that the photon energy becomes sufficient to excite interband transitions, the generated electron-hole pairs are separated by the electric field $E_{SS}$ reducing its value. Decrease of the wavelength leads to an increase in light absorption coefficient and, accordingly, the number of generated electron-hole pairs. As a result, for certain values of wavelength the photovoltage $U_{SS}$ caused by recharging of surface states is reduced to zero.

Calculate the photocurrent density generated when a barrier structure is illuminated. For concreteness, we consider a solar cell with p-type base as a barrier structure (Fig. 7).

![Fig. 7 – Schematic representation of a solar cell](image)

The photocurrent density can be written as

$$J_{ph} = J_p + J_n + J_{SCR},$$

where $J_p$ is the current density of holes generated in n-type region and reached SCR, $J_n$ is the current density of electrons generated in base p-type region and reached SCR, $J_{SCR}$ is the current density of carriers generated within SCR.

Assuming that there is no recombination in SCR, the last term in (12) can be written as

$$J_{SCR} = eF(1-r)\exp(-\alpha x_j)[1-\exp(-\alpha W)],$$

(13)
where $F$ is the flux density of incident photons, $R$ is reflection coefficient, $\alpha$ is absorption coefficient, $x_j$ is the distance from the illuminated surface to the edge of SCR in the n-type region, $W$ is the width of SCR.

To find the $J_n$ and $J_p$ values, it is necessary solving the continuity equations for electrons in the p-region and holes in the n-region, respectively, to obtain the coordinate distributions of these carriers concentrations and neglecting the drift outside SCR to calculate $J_n$ and $J_p$ as diffusion currents of corresponding carriers.

Doing this, we obtain:

$$J_n = e \frac{F(1-r)\alpha L_n}{\alpha^2 L_n^2 - 1} \exp(-\alpha(x_j + W)) \left[ \frac{S_p L_p + \alpha L_p}{L_p D_p} - \exp(-\alpha x_j) \right]$$

$$J_p = e \frac{F(1-r)\alpha L_p}{\alpha^2 L_p^2 - 1} \left[ \frac{S_p L_p + \alpha L_p}{L_p D_p} - \exp(-\alpha x_j) \right]$$

where $D_p$, $D_n$ are diffusion coefficients of holes and electrons, respectively, $L_p$ and $L_n$ are corresponding diffusion lengths. $S_p$ and $S_n$ are surface recombination velocities of holes on the front surface and the electrons on the rear one, $d$ is solar cell thickness (Fig. 7).

In the case of a "semiconductor-metal" or "semiconductor-electrolyte" contact, the photocurrent is caused by separation of carriers generated in SCR, as well as by minority carriers generated in the base region. The SCR edge is situated in that case on the semiconductor surface. Therefore, to calculate the photocurrent density (in the case of p-type semiconductor), we can use the above relations excluding the first term from (12) and taking in (13) and (14) $x_j = 0$. For a n-type semiconductor the parameters $L_n$, $D_n$ and $S_n$ should be substituted by $L_p$, $D_p$ and $S_p$ in (14). Adding (13) and (14), and assuming $d >> L_n$, one can obtain the relation known as the Gärtnert equation:

$$J_{ph} = e F(1 - R) \left( \frac{1 - \exp(-\alpha W)}{1 + \alpha L_n} \right)$$

If we consider the special case of weak absorption, when $\alpha W << 1$ and $\alpha L_n << 1$, the relation (16) can be rewritten as

$$J_{ph} = e F(1 - R)(L_n + W)\alpha$$

Let us introduce the value

$$Y = \frac{J_{ph}}{e F}$$
which is called the external quantum efficiency (EQE) of photoelectrical conversion. In fact, EQE is equal to the number of electrons participating in the photocurrent generation per each incident photon.

Thus, near the absorption edge the spectral dependence of external quantum efficiency to within a constant factor reproduces the spectral dependence of the absorption coefficient. Consequently, it can be used to determine the $E_g$ and $E_U$ values in accordance with the above given relations (2) – (4).

As an example, in Fig. 8 the spectral dependences of external quantum efficiency for CdS films produced by the successive ionic layer adsorption and reaction (SILAR) method are given in the Tauc coordinates $(Y\cdot h\nu)^2 - h\nu$ [3]. It is seen that the obtained spectral dependence of the external quantum efficiency are linearized well in the Tauc coordinates corresponding to direct transitions. Different $E_g$ values for different samples are due to the quantum confinement effect in nanoscale cadmium sulfide.

![Figure 8](image)

**Fig. 8** – Spectral dependences of external quantum efficiency in the Tauc coordinates for the CdS films produced by the SILAR method at 10 (curve 1), 30 (curve 2) and 50 (curve 3) deposition cycles [3]

In Fig. 9, the $\ln(Y) - h\nu$ dependence for the zinc oxide film prepared in [4] by electrochemical deposition is presented. The Urbach energy determined from the slope of plot is equal to $E_U = 196$ meV.

![Figure 9](image)

**Fig. 9** – Spectral dependences of external quantum efficiency for the ZnO film produced by electrochemical deposition [4]
Equation (16) shows that the spectral dependence of the photocurrent can be used to determine the diffusion length of minority carriers. Indeed, the Gärtnern equation can be represented as

$$\ln\left(1 - \frac{Y}{1 - R}\right) = -\alpha W - \ln(1 + \alpha L_n).$$

(19)

According (11b), under applying of a reverse voltage the width of the SCR is proportional to $\sqrt{U_0 + U}$, therefore for $U >> U_0$ the dependence (19) is linearized in $\ln\left(1 - \frac{Y}{1 - R}\right) - \sqrt{U}$ coordinates. In this case, the intercept of an approximating line with the ordinate axis is numerically equal to $\ln(1 + \alpha L_n)$, that allows to determine the parameter $L_n$ knowing the absorption coefficient (Fig. 10).

\[
\ln(1 - Y/(1 - R)) \\
\ln(1 + \alpha L_n)
\]

Fig. 10 – To determination of diffusion length

# Remark 3. If the load resistance, which is connected to the illuminated barrier structure, tends to zero, the photocurrent regime is realized; if it tends to infinity – the photovoltage regime. It can be shown that at low illumination levels (that is usually realized in the experiment) the photovoltage and photocurrent are proportional to each other, therefore to determine the $E_g$, $E_U$ and $L_n$ ($L_p$) values both the photocurrent and photovoltage spectra spectra can be used. ##

**Description of the laboratory setup**

For the measurement of transmission spectra the Proscan MC122 spectrometer is used. This apparatus allows to measure spectra in the wavelength region from 190 to 1100 nm.

The scheme of the setup used for measurement of photocurrent (photovoltage) spectra is presented in Fig. 11.

Incandescent lamp SI-8-200U with a stripe radiating body (the lamp spectrum is shown in Fig. 12) is used as the light source 1. Control of lamp voltage is carried out by digital voltmeter 3 and maintained with an accuracy of 0.01 V that is necessary for stability and reproducibility of the shape of the lamp spectrum.

Light of the lamp is modulated at a frequency of 125 Hz using a mechanical modulator 4. Application of modulated radiation allows the use a narrow-band signal amplification, significantly increasing the signal/noise ratio.

By an optical condenser the light is focused on the entrance slit of grating monochromator MDR-23 with grating 600 lines/mm. For wavelengths above 740 nm the red filter KS-19 is set between the lamp and the optical condenser to cut off the second-order diffracted light. Radiation
on the monochromator output is focused on the studied sample 6 as the strip with a width of 2.2 mm and a height of 6 mm.

The electrical signal is amplified by selective nanovoltmeter with a fixed frequency setting. Basic voltage measurement error of Unipan-237P device expressed as a percentage of reading does not exceed \( \pm \left[ 6 + 2 \left( \frac{U_K}{U} - 1 \right) \right] \% \), where \( U_K \) is the maximal value of the scale for established sub-band, \( U \) is device reading. Input impedance of Unipan-237P equals to 10 M\( \Omega \), output impedance – 560 \( \Omega \) \( \pm \) 10 \%.

Fig. 11 – Block diagram of setup for measuring the spectral dependences of the photocurrent (photovoltage)

Fig. 12 – The lamp spectrum after passing through the optical system
**Tasks and the order of work execution**

Part 1. Measurement and analysis of transmission spectra
1. Acquaint with the user manuals for the Proscan MC122 spectrometer.
2. Switch-on the Proscan MC122 spectrometer and warm up it for 10 – 15 minutes.
3. Measure transmission spectra of the samples under investigation.
4. Analyze measured spectra in order to extract maximal information.

Part 2. Measurement and analysis of photocurrent/photovoltage spectra
1. Acquainted with the scheme of the experimental setup.
2. Turn on the devices and warm-up them.
3. Measure the spectral dependence of the photocurrent of a silicon solar cell.
4. Calculate the energy gap of silicon, Urbach energy, as well as the diffusion length of minority carriers in the base from obtained dependence.
5. Repeat steps 3 and 4 for silicon solar cell irradiated with high-energy electrons. Explain the observed difference between calculated values.
6. Measure the spectral dependence of photovoltage of industrial silicon wafers. Analyzing the shape of the spectrum, to explain the nature of the observed photovoltage.
7. Measure the photovoltage spectrum of p-type silicon wafer, one surface of which has been treated in a polishing etchant $3\text{HNO}_3$: 1HF for 30 seconds, illuminating its treated side. Explain the qualitative change in the shape of the spectrum as a result of etching. Determine the value of the diffusion length of charge carriers in the material.
8. Repeat step 7, illuminating the back side of the etched plate. Compare the spectra obtained under illumination of different surfaces, and explain their differences.

**Test questions**
1. What are the basic mechanisms of light absorption in semiconductors?
2. What is the difference between fundamental absorption in direct band gap and indirect band gap semiconductors?
3. How to determine experimentally the type of the interband transitions (direct or indirect)?
4. How to determine the $E_g$ value from the spectral dependences of the absorption coefficient?
5. What is the Urbach energy and what is its physical meaning?
6. How to determine the $E_U$ value from spectral dependences of the absorption coefficient?
7. What is the mechanism of space charge region formation at the interface between semiconductor and metal (electrolyte)?
8. What conditions must metal (electrolyte) comply for an appearance of the region depleted by the charge carriers in semiconductor?
9. What is the mechanism of photocurrent (photovoltage) generation in the barrier structure?
10. How the spectral dependencies of absorption coefficient and photocurrent (photovoltage) are related to each other?
11. What is the diffusion length of the minority charge carriers?
12. How to determine the diffusion length from spectral dependence of the photocurrent (photovoltage)?

**Instructions for report execution**

The report should contain:
1. Title of the work.
2. Name of students who performed the work.
3. Introduction, where the aim of investigation is formulated.
4. Short summary of the theory explaining the physical nature of the investigated effects, meaning of physical quantities and measured dependencies.
5. Methods of investigation: description of the experimental setup and the objects under investigation, as well as estimation of inaccuracies should be given.

6. Experimental results and their discussion. Based on the experimental data, the main regularities should be marked and physical phenomena underlying them should be analyzed.

7. Conclusions. Critical analysis of the results should be contained here.

**Recommended literature**

**Main**


**Additional**