F3

Photoconductivity of GaP and CdSe:Cr crystals, and InAs/GaAs heterostructures.

The objective of the present experiment is the measurement of the spectrum, as well as the dynamics associated to the photoconductivity in bulk crystals of Gallium phosphate (GaP) and Cadmium selenide doped with chromium (CdSe:Cr), as well as in heterostructures of InAs/GaAs containing quantum dots.

1. **What should you know before attempting the experiment?**
    a. Basic knowledge of solid state physics [1, 2]:
        i. Electronic band structure E(**k**), electrons, holes, effective masses,
        ii. Intrinsic and doped semiconductors, occupancy, electron statystics,
        iii. Transport, mobility,
        iv. Electronic recombination mechanisms, carrier lifetimes,
    b. Photocurrent [2,4]:
        i. Types of optical transitions in a solid, dependency of photocurrent with incident wavelength,
        ii. Changes of free carrier concentration of an illuminated material, dependency of the photoconductivity on the intensity of incident light,
    c. Parameters of CdSr, GaAs and GaP [2, 5, 6]: Band structure, work function, type of gap, effective masses, electronic mobility,
    d. Basic techniques for optical measurements [10, 11]:
        i. Inner workings of a monochromator,
        ii. Lockin-based (modulation-based) measurement techniques.

<u>To prepare for the experiment, you should be familiar with the text below. Special attention should be paid to terms and words in **bold** letters.</u>

In a crystalline solid, electrons are subjected to a periodic potential. Their wavefunction, in this situation, can be described in terms of **Bloch functions**. Free carriers in this material, thus, do not behave as non-interacting electrons in vacuum. Namely, they are not allowed arbitrary energies, have different values of **mass** than their free counterparts, and can possess positive charge. The relationship between the energy E and the quasi-momentum $p = \hbar k$ of electrons in a crystal is also different than that of free carriers in the vacuum. Their dependency $E(k)$ receives the name or band dispersion, or **band structure** (see fig. 1).

In a solid, carriers can inhabit two different types of energy bands: **Conduction and valence bands.** The former is an almost-empty set of energy levels, in which electrons play the role of charge carriers, whereas the latter is an almost-completely-filled set of energy levels in which **holes** act as current-transmitting elements. In insulators or semiconductors, the conduction and valence bands are separated by an **energy gap**. The size (or width) of the energy gap depends on the parameters of the solid, and can have values very close to zero (e.g. in CdHgTe), upwards to over 5 eV (e.g. AlN, diamond). Semiconductors and insulators are different from metals in the aspect that, in the absence of thermal excitations, the conduction band is completely empty, and the valence band is completely filled.

In semiconductors, the energy gap can be classified either as **direct** or as **indirect**. In a direct gap, the minimum of the conduction band happens for the same electronic quasi-momentum k as the maximum of the valence band. In indirect gap, the corresponding maximum and minimum are displaced by a value $\Delta k \neq 0$.

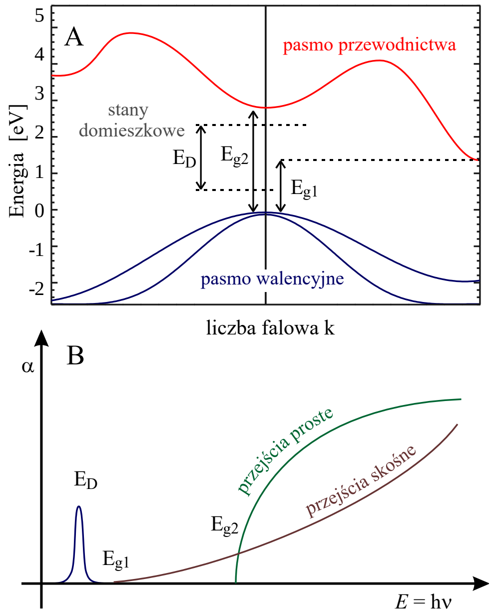


Figure 1 - a) Example of a conduction and valence band for a semiconducting material. b) Associated absorption spectrum. E_D corresponds to states due to impurities (dopants) in the solid.

In a material with a direct band gap, the absorption of light will be dictated by the energy of the incoming photon and the density of states of the bands involved in the absorption event. The absorption coefficient, in this case, can be written as

$$\alpha(h\nu) = A_P \times \left(h\nu - E_g\right)^{1/2} \tag{1.1}$$

Where A_P is a material-dependent parameter.

In indirect-gap semiconductors, the absorption of a photon will invariably involve the introduction (or subtraction) of quasi-momentum to the crystal. The quasi-particle associated with the crystalline momentum introduced to the system is called a **phonon.** In this case, the absorption of an incoming photon will depend not only on the electronic density of states of each involved band, but also on the density of states of the phonons with the momentum necessary to enable the electronic transition. In this case, the absorption coefficient of the material can be written as

$$\alpha(h\nu) = A_S \times \left(h\nu - E_g\right)^{3/2} \tag{1.2}$$

With A_S a material-dependent parameter.

The presence of dopants (impurities) might enable the presence of additional energy states within the energy gap. If optically excited, such states will generate a strong optical response, and the material optical spectra will not only be defined by bulk interband transitions, but also by transitions between impurity bands, as well as transitions between impurity levels and the bulk valence/conduction bands.

The amount of free charges in a material is termed as "**charge carrier concentration**". In a simplistic model, such a parameter is connected to the conductivity of a material through a parameter called **"electronic mobility**" μ. The latter is associated with the velocity, with which charge carriers travel in the solid. The electronic mobility is strongly influenced by the electronic effective mass **m***, which depends on the material considered. If a material has a hole concentration p with mobility μ, its intrinsic conductivity will be approximated by $\sigma = ep\mu$, where e is the elementary electronic charge ($\approx 1.6 \times 10^{-19}$ C). The intrinsic resistivity is defined as $\rho = \sigma^{-1}$.

When irradiated with a light of intensity Φ and energy $h\nu$, the rate at which electron-hole pairs will be generated in a semiconductor is given, on average, by $\Phi\alpha/h\nu$. If the **lifetime** of the excited states is of the order τ, the average charge carrier concentration generated in the material will be given by

$$\Delta n = \Delta p = \frac{\Phi\alpha\tau}{h\nu} \tag{1.3}$$

The employment of $\alpha \neq 1$ is important whenever only few unit cells are considered as contributing to the generation of carriers (i.e. not all incident light is absorbed). If an electric field F is applied to the excited (illuminated) material, a photocurrent will flow through the material

$$I_F = \eta S \frac{\Phi\alpha\tau}{h\nu}(\mu_e + \mu_h)F. \tag{1.4}$$

where μ_e, μ_h is the electronic mobility of electrons and holes, respectively, and S is the illuminated cross-section of the material. The element η corresponds to a parameter termed "**quantum efficiency**" (in principle, always smaller than 1). In equation 1.4, it is assumed that the electronic mobility does not depend on the charge carrier concentration or on the presence of light. It is convenient to remember that the electric field F can be affected by the presence of light in the material, as a consequence of electric screening or due to the ionization of impurities in the material.

The lifetime of carriers of an intrinsic semiconductor is limited by the **electron-hole recombination rate**. In doped semiconductors, however, impurities act as traps which impede recombination. When a semiconductor is illuminated with photons with energy above its energy gap, a large number of free electrons and holes are introduced in its conduction and valence bands, respectively. If the energy of the photon is below the energy gap, however, the excitation happens not between the valence and conduction bands, but rather between the impurity levels/bands and the semiconducting (bulk) band. This process leads to potential fluctuations, as recombination processes should now involve the impurity states (rather than only the valence and conduction bands of the semiconductor). This leads to an extension or shortening of recombination rates in the material. The presence of impurity states can also act as scattering centers and carrier acceptors, which can cause a decrease of the induced photocurrent after an initial increase.

Equation 1.4 is accurate within a condition known as dynamical equilibrium, which occurs for times $t \gg \tau$ after the material has been illuminated. If, for any reason, the relevant relaxation times τ become comparable to the measurement time t, the photocurrent will become time-dependent, following a relation of the type $I_F = I_{F\infty}(1 - \exp(-t/\tau))$, where $I_{F\infty}$ is the photocurrent in the dynamic equilibrium situation.

For the experiments considered here, the incident light will be modulated with a frequency f = 1/T. This means that the sample will be illuminated over a period of time 1/2f, and will be left in the dark for the remaining of the period. The lockin amplifier employed for the measurements measures the difference between averaged values during the illuminated and not-illuminated parts of the cycle. Taking into consideration the exponential character of I_F, the photocurrent measured will be given by I_{FS} (show that this is true!)

$$I_{FS} = I_{F\infty}\left(\frac{1}{2} - \frac{2\tau}{T}\frac{1 - \exp\left(-\frac{T}{2\tau}\right)}{1 + \exp\left(-\frac{T}{2\tau}\right)}\right) \tag{1.5}$$

It is easy to see that, for low frequencies (large T), the photocurrent intensity will be given by $I_{FS} = I_{F\infty}/2$. However, as the frequency is increased, the measured photocurrent intensity will fall, reaching a regime $I_{FS} = I_{F\infty} \times T/8\tau$ for larger values of T. (1.5)

2. Experimental procedure

a. Familiarize yourself with the optical setup, the electronics surrounding it and the computer program controlling everything,
b. Calibrate the monochromator by using the arc lamp and the interference filters provided.
c. Obtain the spectrum of the light source as a function of intensity by using the detectors. The spectrum intensity will be an important parameter to later obtain the efficiency of the material in generating photocurrents
d. Obtain the spectral response (between 500 nm and 1200 nm) of the photocurrent in InAs/GaAs as a function of the light intensity. The light intensity is regulated by controlling the slit size in the output of the monochromator.
e. Obtain the spectral response for the photocurrent of CdSe and GaP for different modulation (chopping) speeds (maintain the intensity constant by setting the monochromator slit to 0.5 mm). The range of interest are 500 nm – 1200 nm for CdSe and 350 nm – 700 nm for GaP.
f. Perform experiments to determine the relaxation time of photocurrents asa function of the wavelength in all samples. For the measurements, we should measure the time-dependence of the signal. The curves should then be fitted through the appropriate function.

3. How to prepare the report

The report should contain the following sections:

1. Abstract,
2. Theoretical introduction,
3. Description of the samples and experimental setup,
4. Results and their analysis,
5. Summary and conclusions, based on the measured data.

Please note that

1. The abstract should consist of a few sentences containing the description of the experiment and its main results,
2. All equations should be justified, and their origins explained,
3. In the description of the experimental setup, the characterization of the monochromator response should be presented. The rspectral response of the interference filters should also be presented. Their peaks are lorenzian, which an be described as $U(E) = A/((E - E_0)^2 + \Gamma^2)$.
4. The experimental results are the spectral responses of the photocurrent obtained at different excitation intensities, as well as measurements of the time-dependence of the photocurrent. The obtained spectra should be corrected by the fact that different wavelengths will show a different light intensity. Once the spectra are obtained, results should be compared with those In the literature, in order to define which spectral signatures are assigned to dopants, which are assigned to quantum dots, which are due to direct gaps, and which are associated with an indirect gap.

   The analysis of the measured spectra shall allow one to define whether photocurrent is proportional to incident power (a plot should be done for a fized wavelength), and to discuss possible mechanisms preventing such a non-linearity (if any)

5. Provide a physical explanation for the observed results.
6. When preparing the presentation, please remember that figures must be correctly labelled (e.g. Fig. 1, 2, 3, etc...), and should be referred by their labels (NOT by "see the figure below"). Figures should be accompanied by a description below the figure. Tables (if any) should also be numbered. However, differently from figures, tables are titled (i.e. the description is atop the table, not below it). Whenever a reference is used, or results from other authors are cited, they should follow with the appropriate reference between brackets (e.g. [1]). The referencing style is up to the author of the report, but should be consistent.

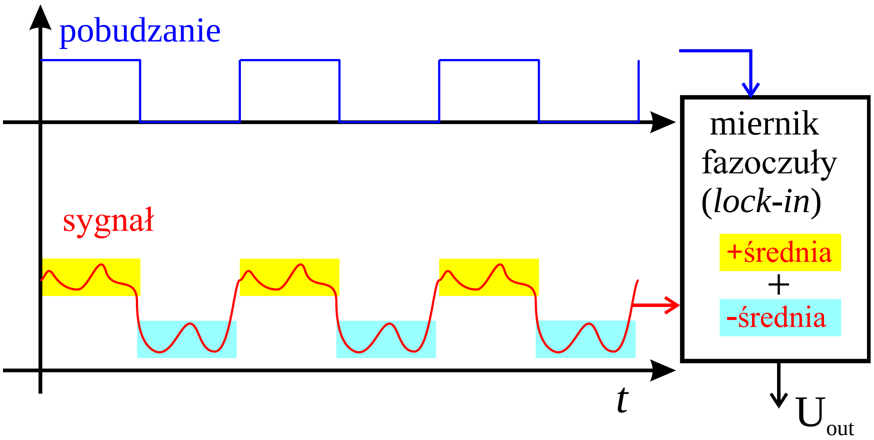
4. Further reading

1. J. Ginter - „Wstęp do fizyki atomu, cząsteczki i ciała stałego."
2. K.W. Szalimowa - „Fizyka półprzewodników"
3. F. J. Blatt – „Fizyka zjawisk elektronowych w metalach i półprzewodnikach"
4. R. Bube - „Photoconductivity in solids"
5. J. Pankove - "Zjawiska optyczne w półprzewodnikach"
6. M. Aven, J. S. Prenner - "Physics and chemistry of II-VI compounds"
7. T. Stacewicz, A. Kotlicki - „Elektronika w laboratorium naukowym"
8. Encyklopedia fizyki lub Wikipedia w wersji angielskiej - hasła: monochromator, kamera CCD.

K.K., R.S., BC 13 IV 2023

Appendix A: phase-locked voltmeter (Lockin)

A phase-locked voltmeter is a device that measures the component of voltage that is modulated to a certain frequency. All other components of the signal (with different frequencies) are disregarded. This allows a very precise noise rejection, by exciting the system with a known frequency and measuring only the system response at the same frequency of the excitation. A visual explanation of the procedure is shown in fig. A1



Rys. A1. Principle of working of a phase-locked voltmeter. The signal (lower curve) is compared with the excitation (upper curve). The excitation is known. The output of the measurement is calculated as the difference between the measured signal during the “0n” cycle (taken as the average of the signal during that period) minus the signal during the “off” cycle. By using this method, all frequencies much larger or much lower than the excitation signal are rejected.

For more information, look at „lockin amplifiers” on Wikipedia, or the encyclopedia of your choice

https://en.wikipedia.org/wiki/Lock-in_amplifier
(last accessed on 08.04.2023)