Physics Lab
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Semiconductors

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Abstract

The energy gap of a semiconductor sample is determined by heating it in a special oven and measuring its resistance as a function of temperature. The bandgap of the semiconductor can be determined by identifying regimes characterized by distinct conduction mechanisms.

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1 Basic knowledge about semiconductors

1.1 What is a semiconductor?

Semiconductors are conductors whose charge carrier concentration (electrons and holes) and therefore the conductivity strongly depends on temperature, as opposed to the electron concentration of metals or insulators.

- Metals do have a high conductivity, $\sigma \approx 10^5\,\Omega^{-1}\mathrm{cm}^{-1}$, which decreases with temperature.
- Insulators do have a very small conductivity, $\sigma = 10^{-14}$–$10^{-3}\,\Omega^{-1}\mathrm{cm}^{-1}$, whose absolute value stays small for all relevant temperatures.
- Semiconductors do have a conductivity in the range of $\sigma = 10^{-12} - 10^3\,\Omega^{-1}\mathrm{cm}^{-1}$ and their charge carrier concentration is strongly dependent on temperature.

The technologically most important representatives of the elementary semiconductors, silicon (Si) and germanium (Ge), are in the fourth group of the periodic system of chemical elements. The atoms are bound by covalent bonds and they form a crystal lattice. There is a huge number of applications and many companies are specialized in semiconductors, starting with Intel Corporation which is the first worldwide manufacturer of semiconductors. Many components of a computer contain semiconductors: microprocessors, graphic processing units, motherboards, etc.

1.2 Energy bands

In order to understand the electronic properties of solids at the atomic level, the Schrödinger equation needs to be considered. The solution to the Schrödinger equation for a single atom leads to discrete energy levels for the electrons. If N such atoms are brought increasingly closer to each other and form a crystal, there is increasing quantum mechanical coupling between the atoms. As a consequence, the energy levels split N times. In a crystal, where N approaches infinity, the energy levels form energy bands of allowed electronic states. This result is obtained by solving the Schrödinger equation, which describes the wave nature of electrons in a crystal. It is of the form

$$\frac{\hbar^2}{2m}\Delta\Psi + (E - V)\Psi = 0, \tag{1}$$

where E is the total energy, V is the potential energy of the electron and m is the free electron mass. The electron spin is neglected here, such that each resulting energy state is spin degenerate. The electrical potential inside the crystal lattice is periodic with the same period as the crystal lattice. Based on this relation, *Bloch* [1] formulated the following Ansatz for the wavefunction Ψ:

$$\Psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}}. \tag{2}$$

This Ansatz classifies states in terms of their wave vector $\vec{k}$ and a band index n. The function $u_{n\vec{k}}(\vec{r})$ has the same period as the crystal lattice.

1.3 Energy states in the valence and conduction bands

The exact form of the periodic potential V in equation (1) is not known. But for the valence electrons, those contributing to the conduction, the kinetic energy is much larger than the potential energy V. The potential V can then be treated as a small perturbation and equation (1) can be solved by perturbation theory. This approximation is known as *approximation for the quasi free electrons*. The most important results are:

- Each state is uniquely labeled by the three quantum numbers $(n, \vec{k}, s)$, where n is the band index, $\vec{k}$ is the wave number and $s = \pm 1/2$ is the spin quantum number.

- The energy $E_{n,s}(\vec{k})$ depends approximately quadratically on $\vec{k}$, the wavenumber, near a conduction band minimum or a valence band maximum. Surfaces of constant energy in $\vec{k}$-space are ellipsoids around these band extrema.

- All values for $\vec{k}$ are allowed but solutions to the Schrödinger equation do not exist at all energies. This explains the appearance of a band gap, i.e. a range of energies, where no electronic states exist. The band scheme for the three different classes of solids is shown in figure 1 [2].

- The density of states (DOS) (the number of eigenvalues per energy unit and volume) close to the bottom of the conduction band and close to the top of the valence band is of the form:

$$D_n(E) = \frac{1}{4\pi^2}\left(\frac{2m_n^*}{\hbar}\right)^{\frac{2}{3}}(E - V_0)^{\frac{1}{2}} \tag{3}$$

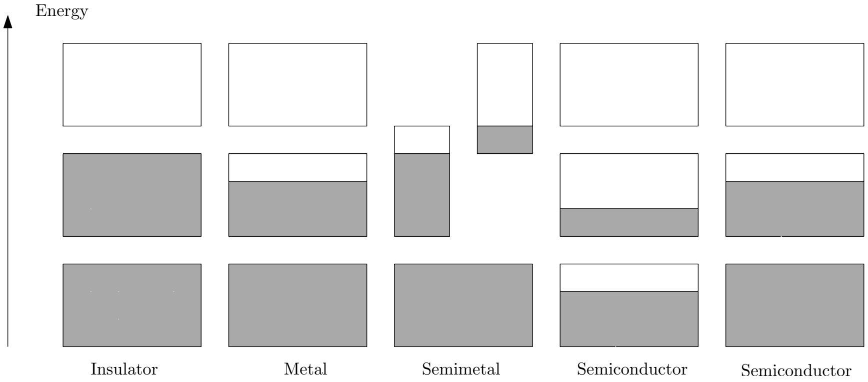

Figure 1: Schematic electron occupancy of allowed energy bands for an insulator, metal, semimetal and semiconductor. The vertical extent of the boxes indicates the allowed energy regions; the shaded areas indicate the regions filled with electrons. In a semimetal one band is almost filled and another band is nearly empty at absolute zero. A pure semiconductor becomes an insulator at absolute zero. The left of the two semiconductors shown is at a finite temperature, with carriers excited thermally. The other semiconductor is electron-deficient because of impurities. Taken from [2].

where $m_n^* = \hbar^2(d^2E_n/dk^2)^{-1}$ is called the effective mass of band n and $E - V_0$ is the absolute value of the energy measured from the conduction band bottom or valence band top.

1.4 Occupation statistics of states

Electrons occupy the energy levels of the valence and the conduction bands. According to the Pauli-principle, each state described by the quantum number $(n, \vec{k}, s)$ can be occupied by not more than one single electron. It is useful to know which levels are occupied at a certain temperature T. The Fermi–Dirac distribution function

$$f(E) = \frac{1}{e^{\left(\frac{E-E_\mathrm{F}}{k_\mathrm{B}T}\right)} + 1}. \tag{4}$$

gives the probability that a quantum state with energy E is occupied at a given temperature T. Here, E_F is the Fermi energy and T is the temperature. For a state at energy E_F, the occupation probability is 50%. In a semiconductor it may happen that no eigenstate $(n, \vec{k}, s)$ exists at which $E_{ns}(\vec{k}) = E_\mathrm{F}$, because E_F may be in the band gap. The Fermi–Dirac distribution is shown in figure 2. The Fermi level is also called chemical potential or in some cases electrochemical potential.

1.5 Metals, semiconductors and insulators

For a $2N$ electron system at $T = 0\,\mathrm{K}$, the N lowest spin-degenerate energy states are occupied. Materials are classified via the position of the Fermi level at zero temperature:

- Metals: E_F lies in the conduction band. Electrons in this energy band can be accelerated by applying an external electric field and therefore contribute to electrical conduction. As a result, metals are good electrical conductors and the temperature dependence of the conductivity is relatively weak.
- Insulators: At temperature zero, the lower energy band, the valence band, is fully occupied and the conduction band is completely empty. The separation in energy between the two bands (band gap) is $\Delta E \gtrapprox 10$ eV. The Fermi energy E_F lies in the band gap, hence is not an actual energy level of the insulator. Since neither completely occupied nor completely empty bands lead to electrical conduction, the material is electrically insulating.

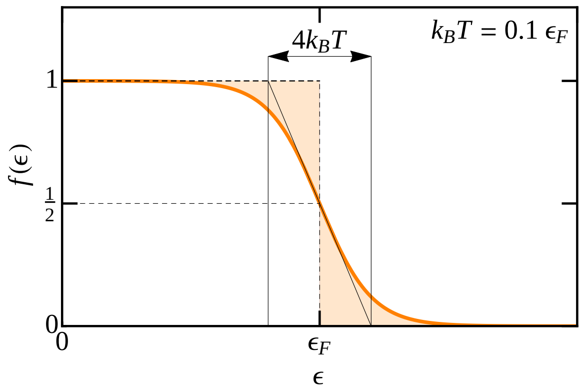

Figure 2: Fermi–Dirac distribution function. It has the value 1/2 at $\epsilon = \epsilon_{\mathrm{F}}$. Its zero temperature limit is a step function at ϵ_{F} with the value 1 for $\epsilon < \epsilon_{\mathrm{F}}$ and the value 0 at $\epsilon > \epsilon_{\mathrm{F}}$ (see dashed line). At finite temperature the step gets softened by temperature. The tangent of the slope at ϵ_{F} cuts the zero-temperature limit at two points with distance $4k_{\mathrm{B}}T$. As a rule of thumb we can therefore say that temperature softens the step by roughly this amount.

- Semiconductors: The energy gap ΔE between valence and conduction band is $\Delta E \lessapprox 10$ eV. An exponentially small number of thermally excited electrons populate the condcution band. The electrical conductivity of the material depends very sensitively on the temperatue via the Fermi–Dirac distribution function.

1.6 The real semiconductor

All previous considerations referred to ideal, so-called *instrinsic*, semiconductors with no lattice defects, no impurities or dislocations. A real semiconductor contains at least $\sim 10^{13}$ impurity atoms per cm^3 (this corresponds to a relative impurity atom concentration of 10^{-10}). Impurity atoms perturb the lattice periodicity and form localized energy states in the band gap. In a voluntarily doped semiconductor, the dopant atoms are chosen from the periodic table of elements such that they have one valence electron more or one less than the native crystal atom that they replace. As a result, they either bind (in the case of acceptors) or donate (in the case of donors) one electron. The energy level of acceptors (donors) is near the valence band (the conduction band).

1.7 Semiconductor structure

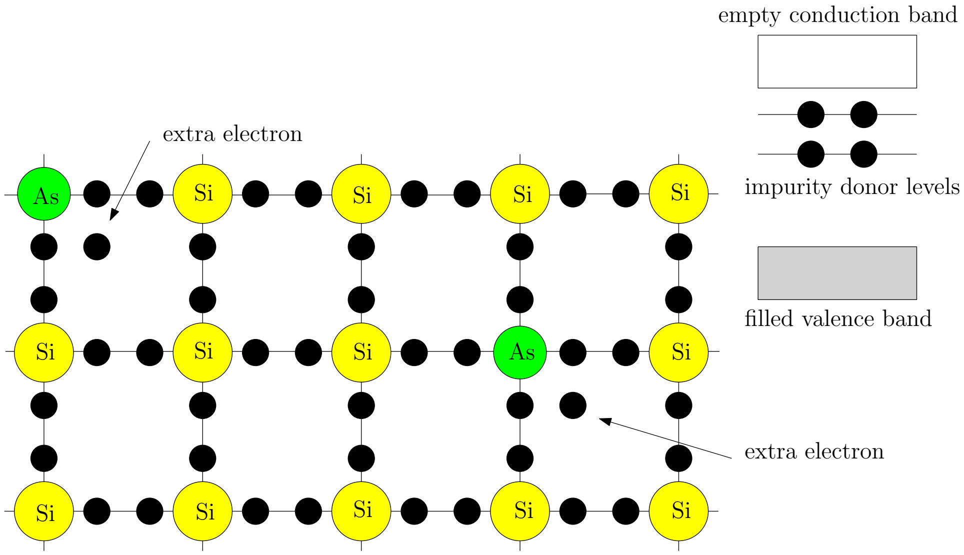

Figure 3: Schematic representation of an n-type semiconductor. Each silicon lattice atom in the diamond lattice has four neighbours. In reality, the atoms sit on the edges of a tetraeder. The impurity atom, here arsenic, donates an additional electron.

1.7.1 n-type semiconductors

Since Silicon is an element of group IV in the periodic table of elements, n-doping can be achieved with donors by replacing an atom in the lattice by an element of group V. The perturbation can be seen as a silicon atom which on the one hand carries an additional positive charge which is localized in the nucleus of the donor and on the other hand contributes an additional electron to the conduction band of the crystal. Figure 3 [3] illustrates the basic idea of an n-type semiconductor in two dimensions. The energy level of the donor atom is in the band gap and close to the conduction band edge of the semiconductor.

1.7.2 p-type semiconductors

Replacing an atom in the lattice by an element of group III (acceptor), the perturbation in the lattice can be seen as a silicon atom with a missing

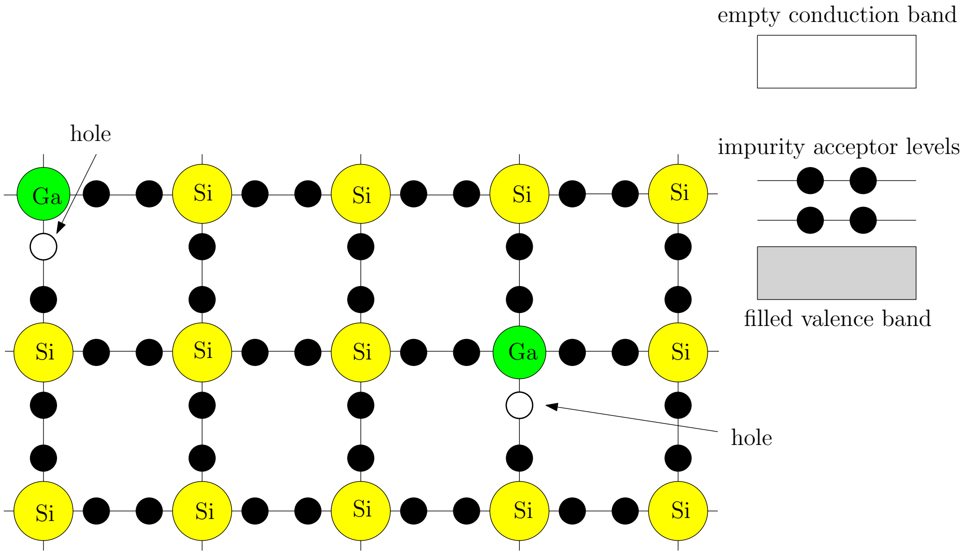

Figure 4: Schematic representation of a p-type semiconductor. Here, silicon is doped with gallium. The gallium atom gives an additional hole (acceptor), which moves in the opposite direction compared to the electron movement.

positive charge in the nucleus of the acceptor and a missing electron in the valence band (also called a 'hole'). Figure 4 [4] shows the basic structure in 2D of a p-type semiconductor. The energy level of the acceptor atom is in the band gap and close to the valence band edge of the semiconductor.

1.8 Intrinsic and extrinsic conduction

The most important property of the donor and acceptor energy levels is that they are very close to the edges of the valence and the conduction bands. Therefore it is much easier to thermally excite an electron from the donor level to the conduction band or to excite a hole from the acceptor level to the valence band, than to excite an electron directly from the valence band to the conduction band. Because of this property, doped semiconductors become conductors even at temperatures, where the thermal excitation is too small to bring an electron directly from the valence band to the conduction band. The resulting conduction in this temperature range is called extrinsic conduction and the semiconductor is said to be extrinsic. Extrinsic conduction strongly depends on the degree of doping. With rising temperature, all donors get ionized and the valence-conduction band excitation becomes dominant. In this regime, the conduction is called intrinsic. Be aware that an intrinsic semiconductor is one without impurities [5].

1.8.1 Charge carrier density in intrinsic semiconductors

- In intrinsic semiconductors, conduction can take place if electrons are thermally excited from the valence to the conduction band. If this happens, not all valence band states are occupied and not all conduction band states are empty. Conduction is caused by electron-hole pairs and the charge carrier density is the same for holes and electrons: $n = p = n_\mathrm{i}$ (n: electron density, p: hole density, n_i: intrinsic charge carrier density).

- The charge carrier density is calculated with the density of states and the probability that these states are occupied by charge carriers (Fermi Dirac distribution f(E)):

  $$n = \int_{E_\mathrm{c}}^{\infty} D_\mathrm{c}(E) f(E) dE = n_\mathrm{i} = p = \int_{-\infty}^{E_\mathrm{v}} D_\mathrm{v}(E)[1 - f(E)] dE \tag{5}$$

  with E_c being the lowest energy level of the conduction band, D_c being the density of states in the conduction band, E_v is the highest energy of the valence band and D_v is the density of states of the valence band.

- Integration under the simplifying assumptions $E_\mathrm{c} - E_\mathrm{F} \gg k_B T$ and $E_\mathrm{F} - E_\mathrm{v} \gg k_\mathrm{B} T$ gives

  $$n = N_\mathrm{c}(T) e^{-\frac{E_\mathrm{c} - E_\mathrm{F}}{k_\mathrm{B} T}} \tag{6}$$

  $$p = N_\mathrm{v}(T) e^{\frac{E_\mathrm{v} - E_\mathrm{F}}{k_\mathrm{B} T}} \tag{7}$$

  with the effective density of states in the conduction (c) or the valence bands (v):

  $$N_\mathrm{c,v}(T) = 2 \left[\frac{2\pi m_{e,h}^* k_\mathrm{B} T}{\hbar^2} \right]^{3/2} \tag{8}$$

- Since $n = p = n_\mathrm{i}$ we have $np = n_\mathrm{i}^2$, and

  $$n_\mathrm{i} = \sqrt{N_\mathrm{c} N_\mathrm{v}} e^{-\frac{E_\mathrm{gap}}{2k_\mathrm{B}}} \propto T^{\frac{3}{2}} e^{\frac{-E_\mathrm{gap}}{2k_\mathrm{B} T}} \tag{9}$$

  and $E_\mathrm{gap} = E_\mathrm{c} - E_\mathrm{v}$.

1.8.2 Charge carrier density in extrinsic semiconductors

The equation

$$np = n_{\mathrm{i}}^2 = N_{\mathrm{c}} N_{\mathrm{v}} e^{\frac{-E_{\mathrm{gap}}}{k_{\mathrm{B}} T}} \tag{10}$$

holds in thermal equilibrium, but the concentration of electrons and holes are not equal anymore. We instead have:

$$n - N_{\mathrm{D}}^{+} = p - N_{\mathrm{A}}^{-} \tag{11}$$

with n: Total electron concentration, given by the intrinsic electron concentration and the electron concentration from donors. N_{D}^{+} : the density of fixed donors that are ionized (correspond to the atoms that gave an electron to n). p: Total hole concentration, given by the intrinsic hole concentration and the hole concentration from acceptors. N_{A}^{-}: The concentration of fixed acceptors that are ionized.

1.9 Electrical conductivity of a semiconductor

In this experiment, three different regimes of the electrical conductivity will be seen when the temperature is raised:

- For very low temperatures ($k_{\mathrm{B}} T \ll E_{\mathrm{gap}}$), no electrons can be excited from the valence to the conduction band, but the dopants can already be ionized (because the energy gap between the doping level and the closest band is smaller than the Si energy gap). Therefore, one expects to have a charge carrier density of the form:

  $$n_{\mathrm{freeze-out}} \propto T^{3/2} e^{-\frac{\Delta E_{\mathrm{D}}}{2 k_{\mathrm{B}} T}} \tag{12}$$

  with $\Delta E_{\mathrm{D}} = E_{\mathrm{c}} - E_{\mathrm{D}}$ for donors and $\Delta E_{\mathrm{A}} = E_{\mathrm{A}} - E_{\mathrm{v}}$ for acceptors.

- There is usually a temperature range ($\Delta E_{\mathrm{D}} \ll k_{\mathrm{B}} T \ll E_{\mathrm{gap}}$) where all dopants have been ionized but intrinsic conduction does not take place yet. Then, the charge carrier density is essentially constant.

- For higher temperatures ($k_{\mathrm{B}} T \approx E_{\mathrm{gap}}$), the intrinsic conduction begins. The charge carrier concentration increases drastically and for $n_{\mathrm{intrinsic}} \gg n_{\mathrm{doping}} = N_{\mathrm{D}}^{+}$ or N_{A}^{-}, one can consider that the charge carrier density is mostly due to intrinsic carriers and use the intrinsic regime equation:

  $$n_{\mathrm{i}} = \sqrt{N_{\mathrm{c}} N_{\mathrm{v}}} e^{\frac{-E_{\mathrm{gap}}}{2 k_{\mathrm{B}} T}} \propto T^{3/2} e^{\frac{-E_{\mathrm{gap}}}{2 k_{\mathrm{B}} T}} \tag{13}$$

- Now the conductivity depends on the charge carrier density n and on the mobility μ according to the relation $\sigma = ne\mu$, where e is the elementary electric charge. In semiconductors, the mobility has generally a bell shape as a function of temperature: for increasing but low temperatures, the mobility increases with temperature because of the increasing thermal energy of carriers. However, for higher temperatures, phonon scattering becomes dominant and the mobility decreases with increasing temperature. This is the case in the intrinsic conduction regime. *Seitz* [6] showed that the mobility has the temperature dependence:

$$\mu \propto T^{-3/2}. \tag{14}$$

- In the intrinsic conduction regime, we therefore find the conductivity to be

$$\sigma = en\mu \tag{15}$$

$$\sigma \propto T^{3/2} e^{\frac{-E_{\text{gap}}}{2k_{\text{B}}T}} T^{-3/2} \tag{16}$$

$$\sigma \propto e^{\frac{-E_{\text{gap}}}{2k_{\text{B}}T}} \tag{17}$$

1.10 Literature

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2 Measurement

2.1 Mounting the sample

The oven should be opened prior to starting the experiment to ensure that the sample is in the correct place and everything is working as it should. When opening up the oven, it is important to wear gloves and handle the fragile equipment with care. Familiarize yourself with the construction used to heat the sample and measure the temperature. Do you understand the purpose of everything you see? The sample has 4 aluminium strip evaporated on the surface to ensure good electrical contact to the wires on the bottom of the sample holder. After making sure that the sample and the thermocouple are in the correct place, the sample holder should be put back into the oven and the pump can be started. The base pressure of the oven should be around 2×10^{-2} mbar.

2.2 Electronic circuit

It is seen from equation (17) that in order to determine the energy gap of the semiconductor sample, its resistance (inverse of conductivity) has to be measured as a function of temperature. The method used in this experiment is called 4 probe measurement.

Problem: Have a look at figure 5, where a schematic circuit diagram is shown. The resistances R_1, R_2, R_3, R_4 represent the cable and contact resistances in the circuit, R_s is the sample resistance and R_V is the internal resistance of the voltmeter, which is very large. With U being the voltage measured by the voltmeter, under which conditions do you find $U \approx R_\mathrm{s} i_0$? (*Hint: The goal is to find conditions under which the cable and contact resistances can be neglected when measuring the voltage and calculating the sample resistance from it.*)

In order to check if the assumptions made to find these conditions are justified in the experiment, check out the 2 point resistance by putting a voltmeter in parallel at the points 1 and 4 of the sample. Compare the obtained resistance with R_V. Based on the results you get, judge whether the assumptions made in order to neglect the contact resistances are justified or not.

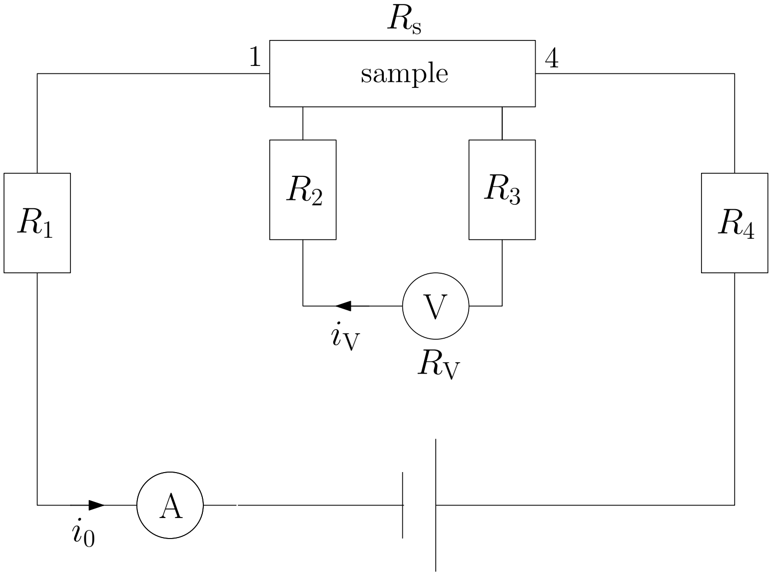

Figure 5: A schematic of the electronic circuit

2.3 Measurement

- Connect the sample as shown on Fig. 5, and check the wiring with your TA before continuing.
- To supply a current to the sample, set the power supply maximum current and adjust the voltage knob to have the desired value of current.
- The current should not be too high in order to prevent the sample from heating up. For this purpose, switch on the temperature sensor attached to the sample in advance and then check for which current the temperature of the sample begins to change. This defines the upper limit for the current.
- Check the 4 probe resistance as a function of the current applied to the sample. When the current is high enough, the resistance does not depend on the current any more. This is the optimal current regime for the experiment. [hint: μA]
- Using the 4 probe measurement, verify that the resistance of the sample is in the order of kΩ, to ensure that the sample is correctly

mounted. Once this is verified, you can continue with the rest of the experiment.

- The sample should be heated up to 600°C. To heat up, turn on the heater, and set the control knob to 80. The oven does not sustain temperatures above 650°C, so remember to reduce the heating power once you reach around 550°C to avoid overheating.
- Then, the sample should be cooled down until the end of the intrinsic regime is reached.
- The measurement consists of taking the values of the current and the voltage across the sample as a function of the temperature. Take approximately one point every 5 K, both when heating up and cooling down.
- Since the resistance changes with the temperature, remember to adjust the voltage of the power supply over time, to keep the current in the correct range.

2.4 Finishing the measurement

For finishing the measurement it is very important that the valve of the vacuum pump is closed *before* the pump is turned off. The sample must *not* see any air at a temperature higher than room temperature! So

- Close the valve of the vacuum pump
- Turn off the vacuum pump
- Turn off electricity
- Remove the wires
- The sample must be left in the oven, until it has completey cooled down to room temperature.

3 Report

Apart from the general guidelines on writing a report given by the VP board, here are the specific recommendations for the report on the semiconductor experiment:

- Introduction: You may discuss the following questions: Why are semiconductors important nowadays? What is special about them? What are the objectives of the experiment here?

- Theory: You may discuss the following questions: What it the difference between metals, semiconductors and insulators? How is the conductivity in a semiconductor defined? What does it depend on? How many regimes can we distinguish for the conductivity, depending on the temperature? What are the different behaviours of the conductivity in these different regimes? What is the relevant regime and the relevant equation for this experiment? Introduce as well the temperature dependence of the semiconductor band gap.

- Experimental setup: You may describe how you did prepare the sample. What does the system consist of and why? What is a 4 probe resistance measurement and why is it employed instead of a simple 2 probe measurement? What is the measurement procedure? What did you especially take care of?

- Results: You may present the graphs and show the different regimes of conductivity if visible. If the curves show an unexpected behaviour, try to find out why. Explain why the measurement results while cooling down should be more accurate than when heating up (therefore use those when estimating the band gap below).

- Analysis: You may perform linear regressions for heating and cooling and discuss the appropriate choice of temperature range for it. Inspect the residuals of the linear regression fit and discuss systematic and statistical errors. Discuss the result for the band gap and compare it to the literature value at the temperature where the measurement has been done. What type of error is dominating? Where can the errors come from? Can we estimate them? Can we try to correct them?

References

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