Determination of the electron effective mass for \textit{n}-type germanium by the low-frequency impedance dispersion

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Abstract. We have proposed and approved a method for calculating the electron effective mass in a semiconductor based on the complex impedance analysis. The electron effective mass for Ge \textit{n}-type (doped by Sb) with a specific resistance of 4 \(\Omega\)-cm (crystallographic directions: [100], [110], [111] and polycrystalline) and 1.5, 7.5, 20 \(\Omega\)-cm (crystallographic direction [111]) are measured. It is shown that the effective mass depends on the impurity concentration and the crystallographic direction.

1. Introduction
Crystalline germanium (mono- and polycrystals) is one of the classical materials for use in optics. The application of germanium in photonics is about 25 – 30\% of the total consumption of this material [1]. Semitransparent mirrors working both without interference coatings, and with them, high-precision Fabry-Perot etalons, acousto-optical elements and other details made from germanium [2–5]. Also, narrow-band interference filters are usually made on Ge substrates.

Impurity germanium crystals are actively used for manufacturing photodetectors recording infrared radiation (IR) [5]. Their work is based on the excitation by a radiation quantum of the charge carrier at the impurity level, passing into the carrierband. For different IR ranges, the appropriate impurity is used. The electrophysical and optical parameters of germanium crystals are correlated. A considerable amount of research of germanium, including optical properties, is carried out by electrophysical methods, which reached considerable perfection in semiconductor electronics. The interrelation between the structure and electrical conductivity (and indirectly, the absorption of radiation) is established not only for single crystals but also for optical polycrystals and for highly pure germanium. The specific electric conductivity of polycrystalline germanium decreases with decreasing crystallite size, which is associated with a decrease in the mobility of charge carriers caused by their scattering at crystallite boundaries. The electrical conductivity in high-purity germanium increases with the decrease in the size of the crystallites, and the lifetime of nonequilibrium charge carriers in it decreases as a result of increase in the concentration of surface electronic states [6, 7].

The newest trend in modern photonics is the creation of new methods of modulation of IR radiation by Ge–based devices, such as modulation by introducing moderate levels of excess carriers in Ge by exciting a diode laser [8]; modulation in waveguide Ge structures on Si substrates by controlling the absorption of free carriers [9, 10]. Ge is a classical semiconductor with a band gap of 0.67 eV [5], hence the effective mass of charge carriers plays an important role in the characterization of its electrophysical properties. At present, the main method for determining the effective mass of charge carriers in a semiconductor is the cyclotron resonance method. At the same time, it characterizes the behavior of free carriers in the field of magnetic forces, whereas in most applications the electric
forces take place. From such point of view, it is of interest to determine the effective mass of free carriers in AC electric field.

2. Research Materials and Methods of the Experiment
We determined the electron effective mass for samples of n-type germanium crystals doped with Sb. Germanium crystals with a diameter of 50–60 mm were grown from the melt by the Czochralski method at Tver State University. Samples of a given crystallographic direction and specific electric resistance were cut from single crystals. Samples under study had the size of 10 × 10 × 5 mm. Charge carrier concentration was determined indirectly using a four-probe method for measuring the electrical resistivity of semiconductors. We used polycrystalline zone-melting purified germanium as a raw material. Doping was carried out with a donor impurity (antimony). With this in view, the doping impurity concentration and the electron concentration are the same.

The corresponding values of the specific resistance (ρ) and the corresponding concentrations of antimony impurities (n), as well as the crystallographic directions of the investigated samples of germanium crystals, are shown in Table 1.

| Specific resistance, (Ω·cm) | Sb concentrations, (cm⁻³) | Crystallographic direction |
|---------------------------|--------------------------|---------------------------|
| 4                         | 3.7·10¹⁴                 | [100]                     |
| 4                         | 3.7·10¹⁴                 | [110]                     |
| 4                         | 3.7·10¹⁴                 | [111]                     |
| 4                         | 3.7·10¹⁴                 | polycrystalline           |
| 1.5                       | 1·10¹⁵                  | [111]                     |
| 7.5                       | 1.7·10¹⁴                | [111]                     |
| 20                        | 8·10¹³                  | [111]                     |

The complex electrical resistance (impedance) of Ge crystals was measured by the LCR method using the Frequency Response Analyzers PSM1735 with Impedance Analysis Interface (Newtons4th Ltd). As electrodes we used two bronze plates between which germanium sample was placed.

The electron effective mass was determined on the basis of analysis of the graphical dependence Z(ω) in the coordinates Z’ and Z” (the Nyquist coordinates), called the Nyquist plot, or the impedance hodograph [11].

3. Results
During the experiments, it was found that the frequency dependences of the impedance strongly depend on the preliminary surface treatment. A comparison of the impedance hodographs with the literature data [11] showed that the measurements of the complex impedance of the polished sample are more correct. Therefore, the measurements used to calculate the dynamic conductivity were carried out for polished samples. As an example, Figure 1 shows the impedance hodograph for Ge sample with a Sb concentrations 3.7·10¹⁴ cm⁻³ (crystallographic direction [100]). The dotted line on a graph shown on a logarithmic scale (Figure 1b) corresponds to the case Z’ = Z”. It should be noted that the Nyquist plots location below this line for all samples under study. According to [12] it means that samples have a universal capacitance and high losses. The impedance hodograph in the normal scale (Figure 1a) has a "classic" semi-circle shape. This allowed us to use it to determine the effective electron mass.

The effective mass was found from the formula for DC conductivity [12]:

\[ \sigma_o = \frac{e^2 n \tau}{m^*}, \]  

(1)
were $e$ – electron charge, $n$ – concentration of charge carriers (in our case – electrons), $m^*$ – electron effective mass, $\tau = 1/\omega_p$ – relaxation time, $\sigma_o = 1/\rho$.

From formula (1), we obtain the expression for electron effective mass:

$$m^* = \frac{e^2 n \tau}{\sigma_o}.$$  \hspace{1cm} (2)

To calculate the relaxation time, the frequency ($\omega_p = 2\pi f$) is determined from the impedance hodograph (Figure 1a), as the frequency of the point corresponding to the maximum value of the imaginary component of the impedance [12, 13]. For the calculations, the specific resistance ($\rho$) and the impurity concentration ($n$) presented in Table 1 were used.

The ratio of the effective electron mass for the germanium samples to the electron mass calculated by formula (2) is shown in Tables 2 and 3. In parentheses the measurement error is given.

**Table 2.** Calculated values of the ratio of the electron effective mass ($m^*$) to the electron mass ($m_e$) for $n$–type germanium samples with a Sb concentrations $3.7 \cdot 10^{14}$ cm$^{-3}$

| Crystallographic direction | relaxation frequency (Hz) | $m^*/m_e$ |
|----------------------------|---------------------------|-----------|
| 100                        | 2.9 \cdot 10^6            | 2.3 (0.2) |
| 110                        | 2.9 \cdot 10^6            | 2.3 (0.2) |
| 111                        | 7.4 \cdot 10^6            | 0.9 (0.2) |
| polycrystalline            | 2.9 \cdot 10^6            | 2.3 (0.2) |

**Table 3.** Calculated values of the ratio of the electron effective mass ($m^*$) to the electron mass ($m_e$) for $n$–type germanium samples for the crystallographic direction [111]

| Sb concentrations, (cm$^{-3}$) | relaxation frequency (Hz) | $m^*/m_e$ |
|-------------------------------|---------------------------|-----------|
| 10 \cdot 10^{14}              | 5.4 \cdot 10^6            | 1.2 (0.2) |
| 3.7 \cdot 10^{14}             | 7.4 \cdot 10^6            | 0.9 (0.2) |
| 2 \cdot 10^{14}               | 2.9 \cdot 10^6            | 2.3 (0.2) |
| 0.8 \cdot 10^{14}             | 2.1 \cdot 10^6            | 3.4 (0.2) |
As can be seen (Table 2), for germanium with the same impurity concentration, the crystallographic direction [111] differs from the others. Along this direction, the effective mass of electrons is smaller. This means that the periodic potential of the crystal lattice along the direction of the charge carriers (electrons) motion corresponding to the crystallographic orientation [111] is significantly different.

This result correlates with the result obtained for the electron effective mass by the cyclotron resonance method, according to which the electron effective masses in germanium in orthogonally directions are greatly different (3.5 and 0.1 $m_e$) [14].

4. Conclusion
Investigations of the electron effective mass in n–type germanium crystals have shown that it depends both on the crystallographic direction in the crystal and on the impurity concentration. For one crystallographic direction, an increase in the impurity concentration leads to a decrease in the effective mass of the electron. Its value approaches the mass of the free electron. Since the increase in the concentration of the donor impurity leads to an increase in the number of electrons in the conduction band, and they occupy higher energy levels, so their behavior in AC electric field approaches the behavior of free electrons.

The difference of the electron effective mass in the crystallographic direction [111] from other directions most probably is explained by the largest distance between germanium atoms in a given direction (relative to the other directions under study).

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