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Hot-Probe method for evaluation of impurities concentration in semiconductors

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Abstract

Electrical, optical, and mechanical properties of thin films significantly differ from those of bulk materials. Therefore, characterization methods for evaluation of thin film properties became highly important. A novel approach to the well known "Hot-Probe" method is proposed and applied in our work. The conventional Hot Probe characterization method enables only the definition of a semiconductor type, P or N, by identifying the majority charged carriers. According to the new Hot Probe technique, one can measure and calculate the majority charged carriers concentration and its dynamic parameters. Feasibility proof of the upgraded Hot Probe method was done in Si and Ge bulk, and in thin film semiconductor samples.

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1. Introduction

The conventional Hot-Probe experiment provides a simple yet efficient way to distinguish between n-type and p-type semiconductors using a heated probe and a standard multimeter. The experiment is done by attaching a couple of cold probe and hot probe to a semiconductor surface. Both probes are wired to a sensitive electrometer [1]. The hot probe is connected to the positive terminal of the meter while the cold probe is connected to the negative terminal. While applying the cold and hot probes to an n-type semiconductor, positive voltage readout is obtained in the meter, whereas for a p-type semiconductor, negative voltage is obtained.

A simple explanation for this experiment is that the thermally excited majority free charged carriers are translated within the semiconductor from the hot probe to the cold probe. The mechanism for this motion within the semiconductor is of a diffusion type since the material is uniformly doped due to the constant heating in the hot probe contact. These translated majority carriers define the electrical potential sign of the measured current in the multimeter. Thus, the hot probe surrounding zone becomes charged with minority carriers and the cold probe remains neutral [2].

Hot Probe experiment may be realized by three various methods:

1. To heat a probe and connect it to the sample under evaluation for a short period while keeping the second electrode (the cold one) constantly connected; variation of the multimeter to the positive or negative direction indicates type of the semiconductor (the old "Hot-Probe" method).
2. To connect two electrodes to the sample under evaluation and heat one of them; this way we obtain information on the type of semiconductor as in the first one and the thermo-electrical voltage dependence on temperature (Seebeck coefficient). This is no matter of the present article.
3. To heat a mediator probe for a pre-defined temperature and attach it to one of the two probes for a certain time. Two electrodes are constantly held attached to the surface. Attachment is maintained until a steady state is obtained. Then the mediator probe heater is removed from the heated electrode. In this way one gets

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additional information concerning the majority charged carriers concentration and the dynamic parameters of the semiconductor material. In our actual work we concentrate efforts on the majority charged carriers concentration only. Dynamic parameters will be discussed in future research.

Generally, the Hot-Probe measurement may be related to as a three-step process. Firstly, the heated probe excites additional charged carriers which are the free charged carriers. This process is different for various materials and various temperatures. Secondly, the warmed majority carriers begin to run from the heated point by a diffusion mechanism. Simultaneously, a built-in electrical field is created between the electrodes. At the same time, the second (cold) electrode also warms. This warming and the built-in electrical field tend to prevent the diffusion process up to a halt at a steady state. This steady state condition carries on until the heat source is disconnected from the electrode. Thirdly, recombination processes of the charged carriers are performed after removal of the heat source.

The above three-step process may be described, in general, by the continuity and Poisson's equations [3]:

$$\begin{cases} \nabla \mathrm{J} + \dfrac{\partial Q}{\partial t} = 0, \\ \nabla \mathrm{E} = \dfrac{Q}{\varepsilon_0 \varepsilon_r}. \end{cases} \quad (1)$$

Here Q is the uncompensated charge density excited by the heated electrode, J is the current density, ε_0 and ε_r are the absolute and relative permittivity, and E is the built-in electrical field. For a theoretical consideration we assume that the semiconductor bulk or thin film samples are positioned on top of a dielectric substrate and they are randomly doped with isotropic properties.

Such as a semiconductor includes two different types of charged carriers: negative and positive, the continuity equation and the Poisson's equation may be divided on two different equations according to the relation:

$$Q = (p - n)q, \quad (2)$$

where p and n are positive and negative charged carriers consequently, and q is an elementary charge.

Before heating (the steady state), the semiconductor sample is in a compensated electro-neutral state, according to the electro-neutrality rule

$$n + N_A = p + N_D, \quad (3)$$

where N_A is the concentration of acceptor ions and N_D is the concentration of donor ions. In the case of extrinsic semiconductor, a p-type for example, the N_D value may be neglected and using the charge conservation law ($pn = n_i^2$), Eq. (3) transforms into the following form

$$p = n + N_A = n_i^2/p + N_A, \quad (4)$$

where $n_i = p_i$ is the intrinsic charged carriers concentration at normal temperature (300 K). The solution of this equation will be

$$p = \frac{N_A}{2} \pm \sqrt{\left(\frac{N_A}{2}\right)^2 + n_i^2}. \quad (5)$$

At higher temperatures, the majority carrier concentration will be differed from (5) on the value n_{iT} only, where $n_{iT} = p_{iT}$ is the intrinsic concentration at T temperature. Heating in one point situated in a distance x from the second (cool) point creates the novel majority carriers concentration p_T. The difference $(p_T - p) = (n_T - n) = \Delta p = \Delta n$ appears to be the thermally excited charge density. These additional charged carriers together with heated majority carriers diffuse from heated electrode area to all directions result in creation of voltage difference. The value $\Delta p = \Delta n$ may be presented as follows:

$$\Delta n = \sqrt{\left(\frac{N_A}{2}\right)^2 + n_{iT}^2} - \sqrt{\left(\frac{N_A}{2}\right)^2 + n_i^2}. \quad (6)$$

Let us assume that the effective mass of the charged carriers and a semiconductor bandgap are stable at the temperature variation from room temperature of up to about 150 °C. So, the intrinsic charged carriers concentration at increased temperature will rise as follows [4]:

$$n_{iT} = A T^{3/2} \exp\left(-\frac{E_g}{2kT}\right) \quad (7)$$

where A is the proportionality coefficient, E_g is a bandgap of the semiconductor, and k is the Boltzmann's constant. This value may be presented using a tabular or known intrinsic concentration at the normal temperature:

$$n_{iT} = n_i \left(\frac{T}{T_0}\right)^{3/2} \exp\left[\frac{E_g}{2kT_0}\left(1 - \frac{T_0}{T}\right)\right] = n_i R \quad \text{and}$$

$$R = \left(\frac{T}{T_0}\right)^{3/2} \exp\left[\frac{E_g}{2kT_0}\left(1 - \frac{T_0}{T}\right)\right], \quad (8)$$

where R is a function of the heating temperature. Thus, Eq. (6) may be rewritten in the following way:

$$\Delta n = \Delta p = \sqrt{\left(\frac{N_A}{2}\right)^2 + n_i^2 R^2} - \sqrt{\left(\frac{N_A}{2}\right)^2 + n_i^2}. \quad (9)$$

This equation may be approximately solved for N_A. Such as $\Delta n < n_i < n_i R$ in our assumptions, one can neglect small values and the solution we obtain is in the following form:

$$N_A \approx \frac{n_i^2 R^2}{\Delta n}. \quad (10)$$

This equation enables an approximate estimation of the impurities concentration in the semiconductor or thin film if measured the additional charge Q. Evidently, the same formula will be obtained for an n-type semiconductor material. This estimation may be verified by an independent measurement of the material resistivity. The main goal of the present work is to prove the proposed theory and apply it to practical measurements.

2. Experimental details

The experimental laboratory setup is shown in Fig. 1. Two spring-loaded Au-coated electrodes placed at a distance of $L = 10$ mm from each other create the closed loop circuit with the digital multimeter. A thermo-couple equipped heater is attached to one of the electrodes to warm it up to 150 °C. A "WS 81" soldering iron of Weller was used also as heater and created a stable controllable temperature up to 450 °C. Voltage and current measurements were carried out using a Keithley automatic test station. The sheet resistance of all samples was measured using a conventional four-point probe station of Cascade Microtech. Silicon and germanium crystalline samples and germanium thin semiconductor films doped with aluminum were studied in the experiment. Germanium thin films were deposited by thermal evaporation. Aluminum powder was attached to the germanium to provide deposition of doped semiconductor coatings. In order to obtain a good Ohmic contact between the electrodes and the sample surface, we used an In–Ga eutectic grout.

The measurement technique was as follows:

A hot electrode was connected to the positive input of a digital voltmeter. Then, the hot electrode was heated up to the required temperature and attached to the sample surface. Measurement was done for 40–60 s approximately and all readouts were stored and analyzed in the computerized Multi Log 710 multimeter of "ExTech".

A current within the closed loop circuit of: multimeter, hot probe, semiconductor film, cold probe and multimeter, is created due to a concentration drop of free charged carriers which generate diffusion within the sample due to the hot probe. There are two optional cases for such closed loops: (a) Ohmic contact between the probe electrodes and the sample surface, (b) blocking contact. In the first case, current is measured and follows the polarities of the measured voltage. In the second case, closed circuit appears as a two back to back diodes pair. Thus, the current is defined by backward saturation current only [5]. The value of this reversed current is very small and cannot be measured by conventional techniques.

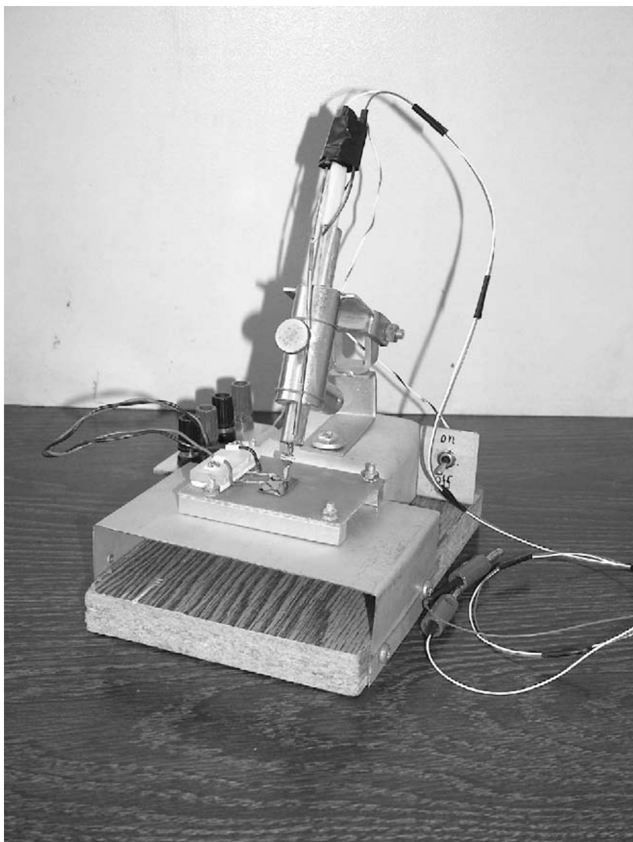

Fig. 1. Experimental laboratory setup for a hot-probe measurement.

3. Results

As the distance of 10 mm between the hot and cold probes is not sufficiently high, the hot electrode conducts heat toward the cold probe on top of the surface plane. In order to check this temperature influence on the second electrode we measured simultaneously the temperatures in both positions of the hot electrode and cold electrode by independent thermo-couple temperature sensors. Fig. 2 presents the obtained temperature characteristics of the cold electrode in various processing times. It can be seen that maximum temperature at the second electrode (cold probe) after ~40 s has not exceeded more than 30 °C, for the highest possible temperature of the hot electrode (450 °C). In lower temperatures, this difference was lower and for 150 °C on the hot electrode, the cold probe temperature was no more of 10 °C. Generally, the maximal variation of the cold point temperature was not more than 6.7% from other hot-probe temperature. Therefore, we may assume that the second electrode temperature deviation can be neglected in the initial stage of measurements and it must be considered farther.

Fig. 3 presents a hot probe characteristics family of curves, measured in a germanium sample for various

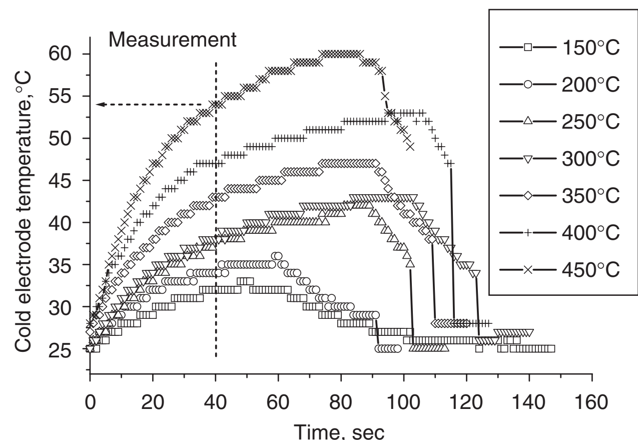

Fig. 2. Cold electrode temperature while measurement.

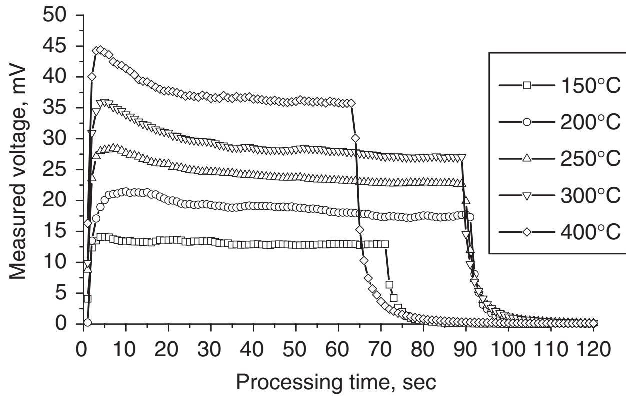

Fig. 3. Hot-probe characteristics for n-type germanium in various temperatures.

temperatures of the hot electrode. These curves show a positive voltage measured between the two electrodes. Therefore, we conclude that the majority carriers in the Ge sample under evaluation are electrons. In other words, this is an n-type semiconductor. The characteristic measurements were repeated for various temperatures. The temperature influence on the obtained curves are found as follows: by increasing the hot-probe temperature, the measured voltage between electrodes was also increased. All curves are similar to each other. Three different regions may be distinguished in the obtained characteristics: (a) a steep rise at the first part, (b) fast decrease to an almost steady state which continues decreasing slowly, and (c) a sharp decrease after removing the heater from the electrode. The slope of voltage decrease in the middle part of the curves is influenced by the cold electrode temperature increase, in our opinion. It is interesting to note that the initial growth and the final decay have the same slopes. This indicates an identity of both physical processes of generation and recombination.

Fig. 4 presents an initial part of the hot-probe characteristic for a germanium chip measured at 150 °C. This figure demonstrates the relationship between the initial state and the steady state. Averaged hot-probe characteristics for a p-type mono-crystal silicon sample and for a p-type polycrystalline silicon sample are presented in Figs. 5 and 6. These characteristics are very similar for various crystal forms of silicon. Fig. 6 shows the voltage and current characteristics measured in the same sample. As shown, the voltage and current curves are almost of the same nature and the conductance of these samples is defined by the conventional Ohm's law.

Hot-probe characteristics for germanium thin films on glass substrates are presented in Fig. 7. These characteristics show measured voltages as a function of heating time for two different temperatures, and shows the same behavior of a semiconductor regardless its type. Obtained films are of p-type and n-type as shown from the negative (a) and positive (b) values of the measured voltages. Increasing of aluminum in the precursor evaporating

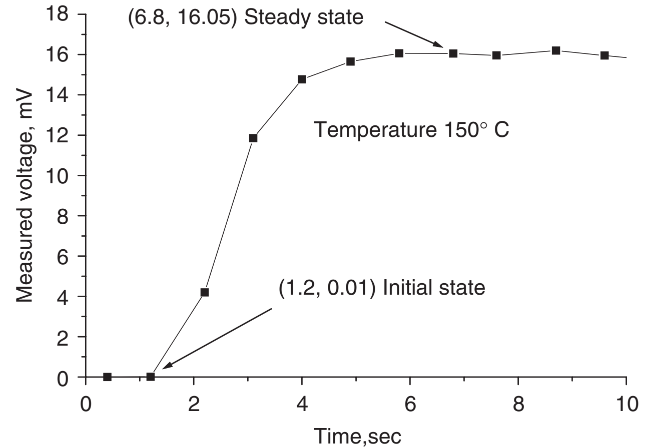

Fig. 4. Hot-probe characteristic of germanium, measured at 150 °C.

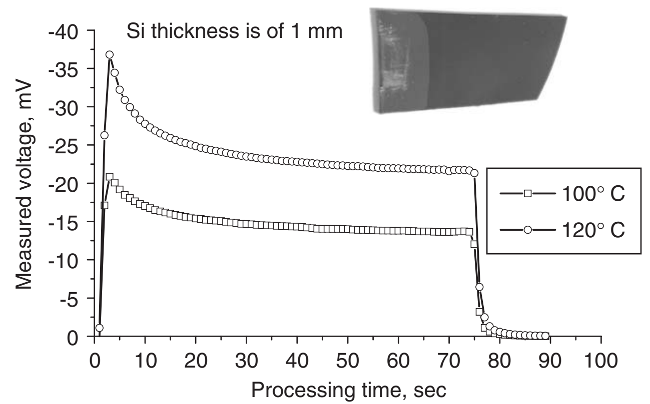

Fig. 5. Averaged hot-probe characteristics for p-type silicon sample.

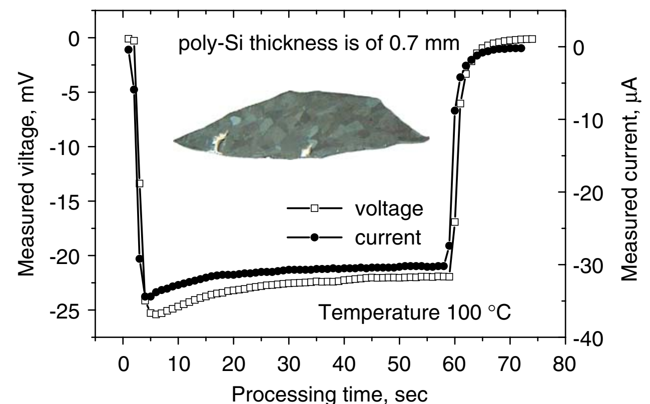

Fig. 6. Averaged hot-probe characteristics for p-type polycrystalline silicon sample.

material changes the sign of the majority charge carriers in the grown germanium film. Comparing hot-probe characteristics measured for bulk, and thin film semiconductor materials (see Figs. 3, 5–7) demonstrates that these materials behave the same way irrespective of their crystal structure and/or thickness. Thus, the same measurement

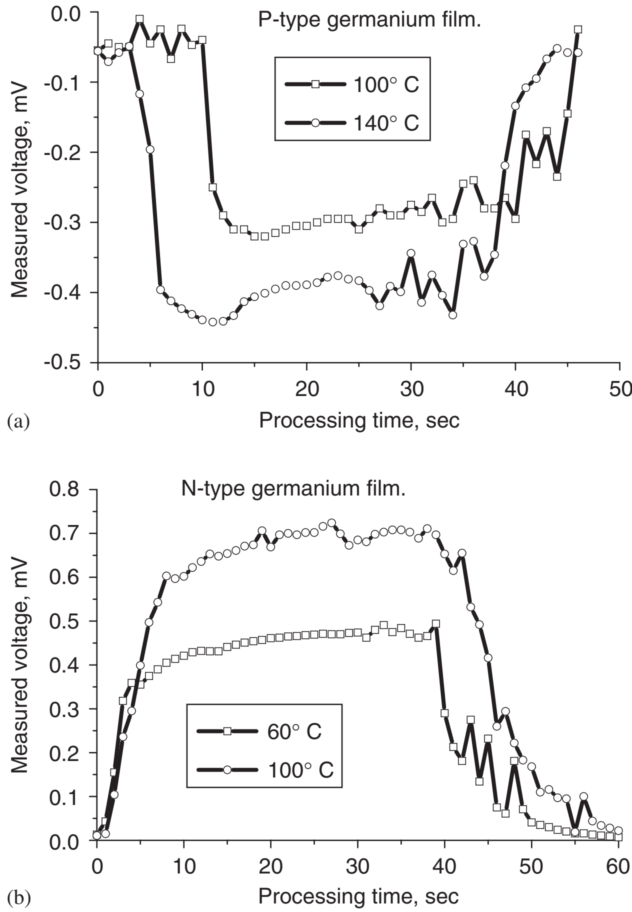

Fig. 7. Hot-probe characteristics for germanium thin films doped with aluminum during deposition in glass substrates: (a) p-type film, (b) n-type film.

and calculation methods may be applied to characterize thin semiconductor films regardless of the growth method.

4. Discussion

The hot excited charged carriers begin diffusing from the hot probe at all directions meaning half sphere or 2π steradians. This diffusion process obeys the Fick law. In a constant heating temperature, the diffusion process resembles the diffusion from a defined source. The hot charged carriers leave the heated zone and create a depletion region around the hot probe. Thus, the diffusion equation may be written in one-dimension as follows:

$$\int_0^\infty N(x,t)\,\mathrm{d}x = Q, \tag{11}$$

where $N(x,t)$ is a concentration of the free charged carriers in distance x and time t. The solution of Eq. (11) is in the well known Gaussian form:

$$N(x,t) = \frac{Q}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right). \tag{12}$$

Here D is the diffusion coefficient of the charged carriers. Now, using the relation $Q = qN(x,t)$ the Poisson's equation (1) takes the following form:

$$\frac{\partial E}{\partial x} = \frac{q}{2\pi\varepsilon_0\varepsilon_r}\frac{Q}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right). \tag{13}$$

If we designate

$$B = \frac{q}{2\pi\varepsilon_0\varepsilon_r}\frac{Q}{\sqrt{\pi D t}}, \quad y^2 = \frac{x^2}{4Dt} \quad \text{and} \quad \mathrm{d}x = 2\sqrt{Dt}\,\mathrm{d}y,$$

Eq. (13) becomes:

$$\frac{\partial E}{\partial x} = B \cdot e^{-y^2} \tag{14}$$

which is a classic equation that cannot be solved using elementary functions [6]. However, the right part of Eq. (14) may be represented in a series form for $y<1$:

$$e^{-y^2} = 1 - \frac{y^2}{1!} + \frac{y^4}{2!} - \cdots + (-1)^2\frac{y^{2n}}{n!}. \tag{15}$$

In our case, for $x = L = 1\,\text{cm}$ and a time of 5–10 s at temperatures of 300–423 K, $y<1$. Therefore, Eq. (14) may be integrated partially

$$\frac{E}{2\sqrt{Dt}} = B\int_0^y e^{-y^2}\,\mathrm{d}y = By - B\frac{y^3}{3} + B\frac{1}{2}\frac{y^5}{5} - \cdots. \tag{16}$$

The voltage V measured between the hot probe and the cold probe may express from E by integration of the equation

$$\frac{\partial V}{\partial x} = -E. \tag{17}$$

Thus, (17) may be integrated using (16) as

$$\frac{V}{2\sqrt{Dt}} = -B\frac{y^2}{2} + B\frac{y^4}{12} - \cdots. \tag{18}$$

After neglecting all small components and re-substitution, we obtain the following expression:

$$V = -\frac{q}{2\pi\varepsilon_0\varepsilon_r}\frac{Q}{\sqrt{\pi}}\frac{x^2}{4Dt}. \tag{19}$$

The additional charged carriers quantity may be obtained from this equation for $x = L$:

$$Q = -\frac{V \cdot 2\pi^{3/2}\varepsilon_0\varepsilon_r \cdot 4Dt}{qL^2}. \tag{20}$$

In first approximation, the diffusion coefficient value may be calculated using the well known Einstein equation and tabular value of the charged carriers mobility for a given temperature. The sign of Δn is defined by the type of

material. Calculations according to formulae (20) and (10) will obtain the majority charged carriers concentration.

5. Application of the hot probe method

The type of the semiconductor material is defined in the old "Hot-Probe" method by the sign of the measured voltage. A thermo-electric power (Seebeck's coefficient) may be calculated from measurements of the voltage at various temperatures. For example, in order to build the relationship of thermoelectric power and temperature, we use Fig. 3. Maximum value of the voltage should be related to the temperature. The angle of slope of the graphical characteristics is equal to the thermoelectric power. To estimate the majority charged carriers concentration, (8), (10) and (20) should be applied.

Estimation of the majority charged carriers was done for Ge sample, n-type. Its hot-probe characteristic is presented in Fig. 4. As shown, the sample was measured by hot-probe at 150 °C. A time interval between the initial state and steady state was of 5.6 s, and the maximal measured voltage was 16.04 mV. Additional data for the Ge sample were taken from Ref. [7]: $E_g = 0.66\,\text{eV}$, $\mu_n = 3900\,\text{cm}^2/\text{V s}$, $n_i = 2.4 \times 10^{13}\,\text{cm}^{-3}$, $\varepsilon_r = 16$. Calculation accordingly presented theory results as the following values $R = 66.3$, $\Delta p \approx 5 \times 10^9\,\text{cm}^{-3}$, and $N_D \approx 2.5 \times 10^{21}\,\text{cm}^{-3}$ which agreed with a direct resistivity measurement.

6. Conclusion

A novel approach to the well known hot-probe method was proposed. The novel approach consists of measurement of the thermo-generated voltage between heated and cold electrodes along a heating and relaxation periodic cycle. Obtained experimental curves are analyzed. Using mathematical results we are able to calculate the majority charged carries concentration in bulk semiconductors or thin film semiconductors. It means that this renovated Hot-Probe method should become a prevalent method for operative evaluation of semi-conducting samples and semiconductor thin films.

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