Fyzikálny časopis 20 (1970), No. 1

INFLUENCE OF NEUTRON RADIATION ON THE CHARACTERISTIC QUANTITIES OF THE ALLOYED SEMICONDUCTOR GeSi

PAVEL MACKO, Bratislava

The paper deals with the measuring of the conductivity, the Seebeck coefficient, the thermal conductivity and the Z-parameter of five samples of the n-type GeSi in the range of temperature between 100–400 °K, which samples ware irradiated at 300 °K with fast neutrons by doses of 0, 1 . 10^{16}, 1 . 10^{17}, 5 . 10^{17} and 1 . $10^{18} n'$. cm^{-2}. The experimental values are given in relatively simple expressions. There were found negative changes of all investigated parameters, which begin to manifest themselves in cases where the concentration of the defects N'_D is greater than the concentration of the inherent defects N_{D_0} before the irradiation.

INTRODUCTION

The radiation damages in the semiconductor due to bombarding by fast neutrons result in changes of practically all characteristic parameters of the material. The sensivity of the material to the radiation damages is the greater the more homogenous – single crystallike – the semiconductor is, with the lowest possible number of primary imperfections. A great number of works studies the changes of some physical parameters of semiconductors in dependence on the intensity of the integrated dose of radiation of the fast neutrons, while they neglect the changes of physical quantities, which are characteristic for semiconductor thermomaterials. And it is the semiconductor thermomaterial which could be utilized when converting the secondary thermal energy of reactors into electrical energy. That is why in the present paper we investigate the influence of the neutron radiation on the characteristic parameters of an alloyed GeSi semi-conductor, which are included in the definition of the Z-parameter:

$$Z = \frac{\alpha^2 \sigma}{\lambda}, \tag{1}$$

where α – the Seebeck coefficient, σ – the conductivity coefficient, and λ – the thermal conductivity coefficient.

The alloyed Ge Si material is a semiconductor, considered for the construction of thermo-piles, or semiconductor refrigerators. It is manufactured because of its good qualities:

1. A great value of the efficiency coefficient of the conversion of thermal energy to electrical energy even at high temperatures.
2. A great mechanical strength.
3. A high melting point (1250 °C).
4. A low team pressure.
5. A resistance to atmospheric oxidation.

MEASURED SAMPLES AND THE USED MEASURING METHODS

The influence of neutron radiation was investigated on samples of the GeSi n-type, doped with P, with a 71.3 % content of Si in the samples. From such a material there were preparated five samples of size 20×8×3.3 mm, which had at the temperature of 300 °K the following values of the investigated parameters: $\alpha = 500\ \mu\text{V} \,.\, \text{deg}^{-1}$; $\sigma = 7.2\ \Omega^{-1}\text{cm}^{-1}$; $\lambda = 5.3 \times 10^{-2}\ \text{W cm}^{-1}\text{deg}^{-1}$; $Z = 0.31 \times 10^{-4}\ \text{deg}^{-1}$; free carriers concentration $n = 2.8 \times 10^{17}\ \text{cm}^{-3}$; free carriers mobility $u = 171\ \text{cm}^2\ \text{V}^{-1}\ \text{sec}^{-1}$; Debye temperatures $\Theta = 520$ °K.

The samples were irradiated with fast neutrons of an energy of 2 MeV in the reactor at the Ústav jaderného výskumu ČSAV in Praha-Řež in this way: sample 1 was not irradiated, sample 2 was irradiated with the integral flux $\Phi_2 = 1^6 \times 10^1\ \text{n'cm}^{-2}$, sample 3 was irradiated with the flux $\Phi_3 = 1 \times 10^{17}$ n'cm^{-2}, sample 4 with the flux $\Phi_4 = 5 \times 10^{17}\ \text{n'cm}^{-2}$ and samle 5 was irradiated with the flux $\Phi_4 = 1 \times 10^{18}\ \text{n'cm}^{-2}$. The temperature during the irradiation was 300 °K.

We measured the changes of the investigated parameters in dependence on the neutron radiation dose and the temperature.

With the non-irradiated GeSi semi-conductor dealt the authors of paper [1].

The alloyed semiconductor GeSi is a homogeneous material of a polycrystalline character. The damages, which originate from the interaction of the bombarding neutron with the atoms of the semi-conductor, are distributed regularly throughout the whole volume of the sample. In most cases they have the character of vacancy clusters, intercentres or wedges of displacement. The influence of the radiation damages is negative, because they reduce the concentration of the free carriers of change by compensation and they increase their scattering.

For the measurement of the investigated parameters we use the twin-lead measuring methods, which are described in details in papers [2] and [3]. Simply by changing the function commutator of the pulse generator we measured by turns the conductivity σ and the quotients α^2/λ and α/λ. Then from the measured values we calculated the values of the investigated parameters.

Every sample was fixed in a separate holder (Fig. 1). The samples had two cross slots engraved by a ultrasonic cutter, which were filled by a Ga-solder. Then the measuring wires of the device were forced into the slots. The sample fixed on such a device was able to get into the cryostat in a very simple way.

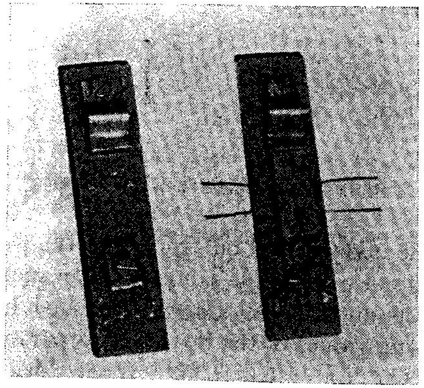
Fig. 1. Measured samples holder.

In all samples their Hall-constant and conductivity in the magnetic field was measured at room temperature.

RESULTS OF MEASURING

In Table 1 there are the results calculated from the measurements of the Hall-constant and the conductivity in the magnetic field with the induction $B = 1$ T. The graphical description of the courses of $n = f_1(\Phi)$ and $u = f_2(\Phi)$ at $T = 300$ °K are in Fig. 2. From Table 1 and also from the graph courses it is evident that the determining parameter is the change of concentration of the free carriers of charge, which after the irradiation with the dose $\Phi = 1 \times 10^{18}\,\mathrm{n'cm^{-2}}$ changes by about three orders, while their mobility changes only by about one order.

Table 1

No	$\Phi[\mathrm{n'cm^{-2}}]$	$\Omega[\sigma^{-1}\mathrm{cm^{-1}}]$	$R_H\left[\frac{\mathrm{cm^3}}{\mathrm{A\ sec}}\right]$	$n[\mathrm{cm^{-3}}]$	$n\left[\frac{\mathrm{cm^2}}{\mathrm{V\ sec}}\right]$	$N'_D[\mathrm{cm^{-3}}]$
1	0	7.22	22.08	2.83×10^{17}	171.2	0
2	1×10^{16}	4.83	25.2	2.48×10^{17}	124	2×10^{16}
3	1×10^{17}	1.28×10^{-2}	3.4×10^{3}	1.83×10^{15}	43.6	2.7×10^{18}
4	5×10^{17}	1.2×10^{-3}	2×10^{4}	3.13×10^{14}	24	1.6×10^{19}
5	1×10^{18}	8×10^{-4}	2.5×10^{4}	2.53×10^{14}	19.7	2×10^{19}

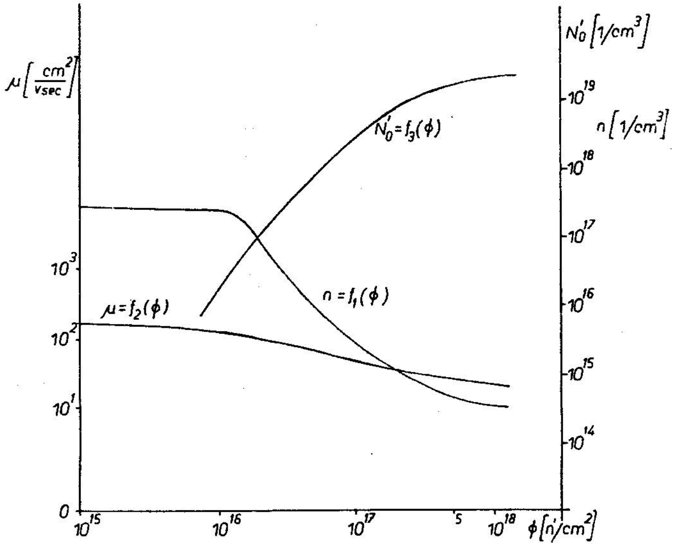

Fig. 2. Flux dependences of free charge carriers mobility (u), of radiation defects concentration (N'_D), and of free charge carriers concentration (n).

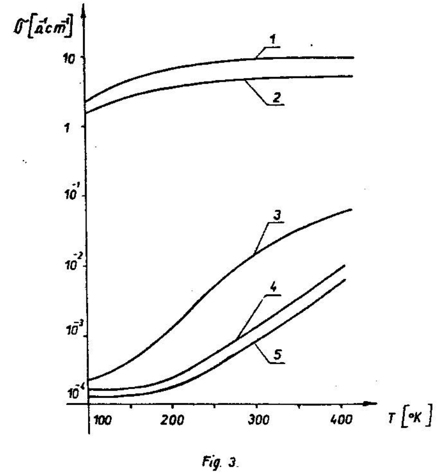

Fig. 3. Temperature dependences of electrical conductivity for the samples 1, 2, 3, 4, 5.

All the investigated quantities were measured in the interval of temperature 100—400 °K. The measured values are plotted in the graphs with solid lines. In Fig. 3 there are plotted the dependences of conductivity on temperature $\sigma = f_\sigma(T)$, Fig. 4 shows the dependence of the Seebeck-coefficient on temperature $\alpha = f_\alpha(T)$, Fig. 5 shows the temperature dependence of the thermal conductivity $\lambda = f_\lambda(T)$ and Fig. 6 there is the dependence of the Z-parameter on the temperature $Z = f_Z(T)$, for the irradiated samples as well as for the non-irradiated one. The measurments showed that radiation damages have a negative influence on all investigated parameters. For samples 4 and 5 could not measure all parameters due to their high specific resistance.

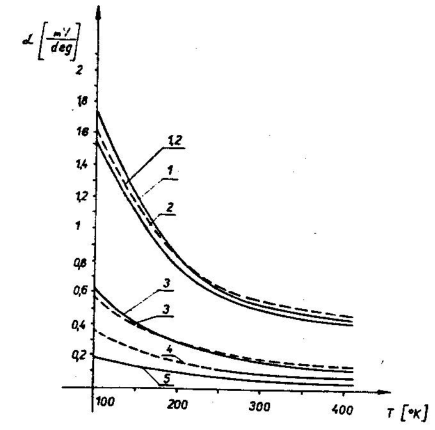

Fig. 4. Temperature dependences of the Seebeck coefficients for 5 samples. Solid lines represent experimental curves, dotted lines are theoretical curves.

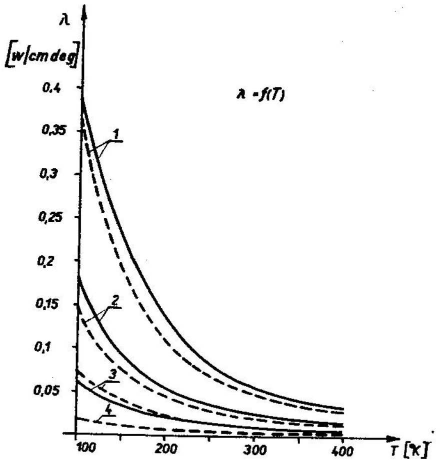

Fig. 5. Temperature dependences of the thermal conductivity. Solid lines represent experimental curves, dotted lines are theoretical curves.

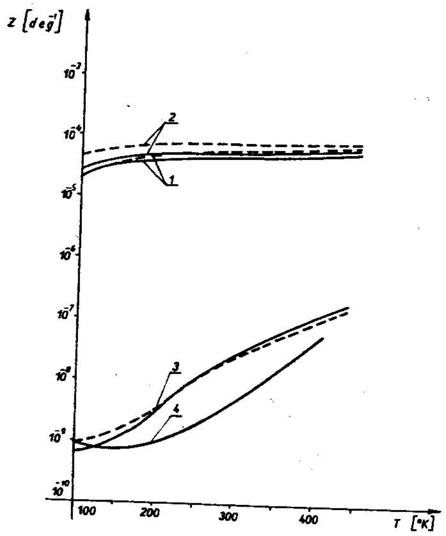

Fig. 6. Temperature dependences of the Z-parameter. Solid lines represent experimental curves, dotted lines are theoretical curves.

DISCUSSION AND THEORETICAL INTERPRETATION OF EXPERIMENTAL VALUES

A. *Electrical conductivity*

From the Boltzmann equation for the electron conductivity of the n-type semiconductor, in the case of an ideal semiconductor with spherical surfaces, the following relation follows:

$$\sigma = \frac{K_{1,2} \exp\left(-\Delta E_{1,2}/2kT\right)}{AT^{3/2} + BN_D T^{-3/2}} \tag{2}$$

where for the zone of additional conductivity (low temperatures) we have

$$K_1 = 2^{-1/2} e (A_n N_d)^{1/2} \quad \text{and} \quad \Delta E_1 = \Delta E_d \tag{3a}$$

and for the zone of intrinsic conductivity high temperatures we have

$$K_2 = e (A_n A_p)^{1/2} \quad \text{and} \quad \Delta E_2 = \Delta E, \tag{3b}$$

where A and B are numerical coefficients, N_D is the total concentration of the defects in the semiconductor, A_n and A_p are effective densities of states of concentration of donors, or holes.

In our specific case a mechanism of the intrinsic conductivity begins to dominate in the material of the semiconductor above 180 °K.

From expression (2) it follows that the influence of the neutron radiation and the defects resulting from it, at constant temperature (in the case when $AT^{3/2}$ is negligible), can be approximated by the expression

$$\sigma = \frac{\text{const}}{N_D}. \tag{4}$$

The total concentration of defects in the semiconductor can be expressed in the form

$$N_D = N_{D0} + N'_D, \tag{5}$$

where N_{D0} is the concentration of the defects in the non-irradiated material and N'_D is the concentration of the defects, formed by neutron irradiation, hence the electrical conductivity can be expressed in the form

$$\sigma = \frac{K}{1 + N'_D/N_{D0}}. \tag{6}$$

This expression for $N'_D \gg N_{D0}$ is simplified as follows:

$$\sigma = K\frac{N_{D0}}{N'_D}. \tag{7}$$

This course of the dependence is in good agreement with the measured course. For the constants K and N_{D0} we found these numerical values:

$$K = 5.1\ \Omega^{-1}\mathrm{cm}^{-1}$$

$$N_{D0} = 4 \times 10^{15}\ \mathrm{cm}^{-3}.$$

For the concentration of radiation defects, we obtained using the results of paper [4] the expression:

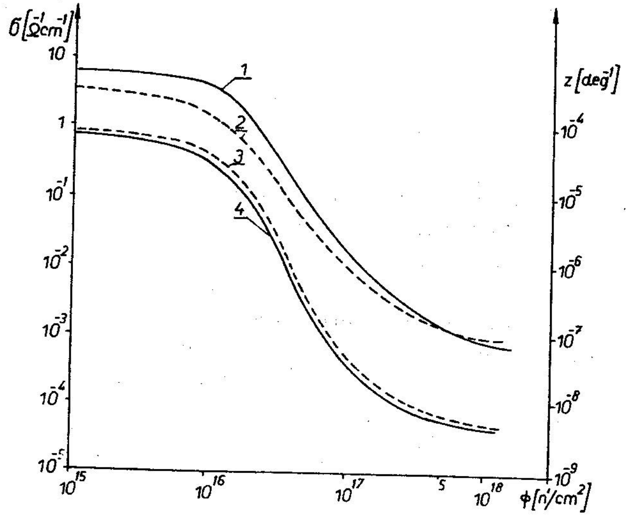

Fig. 7. Flux dependences of the electrical conductivity and of the Z-parameter at $T = 300$ °K. Curve 1 represents experimental courses and curve 2 theoretical courses of the electrical conductivity. Curve 3 represents experimental courses and curve 4 theoretical courses of the Z-parameter.

$$N'_D = \frac{5 \times 10^{33}\ \mathrm{cm}^{-6}}{n}, \tag{8}$$

where n is the concentration of the free carriers of charge.

The concentrations of the radiation defects N'_D in dependence on the integral dose of the neutron irradiation, or the concentration of the free carriers of charge are in Table 1.

The values of conductivity, calculated from the relations (7) and (6), are in good agreement with the experimental results. For the sake of comparison there are plotted in the graphs in Fig. 7 the experimental as well as the theoretical values of electrical conductivity as a function of the dose of neutron radiation. The influence of the formed defects N'_D will be evident from the change of the investigated parameters only in the case when $N'_D > N_{D0}$.

From the courses of the plotted dependence in both Fig. 7 also Fig. 3 we can see that the total decrease of the elecrrical conductivity is due to the neutron flux Φ from the interval $\langle 10^{16} - 10^{18} \rangle$ n′cm^{-2}. Before, as well as after this interval the electrical conductivity changes are only very small. We arrived at similar conclusions in paper [5], too.

B. *The Seebeck coefficient*

In solving the dependences $\alpha = f_\alpha(\Phi, T)$ we started from the general expression for the Seebeck coefficient:

$$\alpha = -k/e[(r + \tfrac{5}{2}) - E_F/kT], \tag{9}$$

where r is the coefficient of scattering and E_F is the energy of the Fermi level. The value of the Fermi energy depends on the concentration of the carriers of charge N_d, or n, or indirectly on the concentration of the radiation defects N'_D respectively, according to the well-known theory, see [6].

In order that the expression for the Seebeck coefficient may express at the same time not only its temperature dependence but also the influence of the neutron radiation, we can express it by the relation

$$\alpha = k_n^m G \alpha_0, \tag{10}$$

where the coefficient k_n^m expresses the dependence of the Seebeck coefficient on the dose of neutron radiation by the expression

$$k_n^m = -\Delta\alpha/\Delta\Phi, \tag{11}$$

where the exponent m from the expression (11) has the form

$$m = \log \frac{\Phi}{\Phi_0} \qquad (12)$$

and Φ_0 expresses numerically the lower boundary dose of neutron radiation.

The factor G from the expression (10) is a material constant, of which the numerical value is defined so that at the given temperature the measured value of the Seebeck coefficient may be in agreement with the theoretical value. According to the given conditions the numerical factors in case of the alloyed semiconductor GeSi have these values: $k_n = 0.337$ V cm^2 n$'^{-1}$deg^{-1}; $G = 2.6 \times 10^{-2}$ n'deg V^{-1} cm^{-2}; $\Phi_0 = 1 \times 10^{16}$ n'cm^{-2}.

The concrete form of the ralation (10) which expresses the material characteristics of GeSi is

$$\alpha = 2.6 \times 10^{-2} \times 0{,}337^{\log 10^{-16}\Phi} \times \alpha_0. \qquad (13)$$

The values of the Seebeck koefficient $\alpha = f'_\alpha(T)$ calculated from the given relations are plotted into the graphs in Fig. 4 With a dotted line. The small deviations between the courses of α_{theor} and α_{exp} are probably due to the change of the numerical value of the scattering coefficient, which was constant in our computations.

The values of the Seebeck coefficient as a function at the T = const. are plotted in the graphs in Fig. 8.

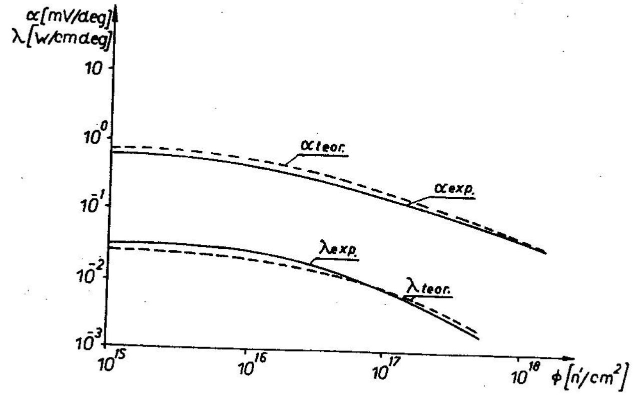

Fig. 8. The curves represent experimental and theoretical flux dependences of the Seebeck coefficient and of the thermal conductivity coefficients.

C. *Thermal conductivity*

The total thermal conductivity λ is expressed by the relation:

$$\lambda = \lambda_e + \lambda_m, \qquad (14)$$

where λ_e is the electron component of the thermal conductivity and λ_m is its lattice component.

If we neglect the electron component of the thermal conductivity λ_e, which usually represents in the case of semiconductors only the correction of the total thermal conductivity, we get according to Peierls for thermal conductivity the expression:

$$\lambda^{-1} = R_1 T^y \exp\left[-\frac{\Theta}{T}\right] + R_2 N_D T^z, \qquad (15)$$

where R_1 and R_2 are the numerical constants, y and z are the numerical values. The expression (14) does no more contain the component of thermal conductivity conditioned by the reflex from the edges of the crystalline grains, because this manifests itself only for $T < 100$ °K.

We are looking for a dependence of the changes of thermal conductivity on the concentration of defects of N_D, or N'_D resp. That is why we express (15) in such a way that the influence of the defects caused by neutrons on the changes of total thermal conductivity may be clearly evident:

$$\lambda = \left\{R_1 T^y \exp\left[-\frac{\Theta}{T}\right]\left[1 + \frac{R_2 T^z N_D}{R_1 T^y \exp(-\Theta/T)}\right]\right\}^{-1}. \qquad (16)$$

Since the number of defects N_D in the irradiated semiconductor is very high we can neglect 1 in square brackets compared with second member and after rearrangement we get for the thermal conductivity the expression:

$$\lambda = \frac{R'_2}{b} \cdot \frac{T^{-z}}{N_{D0} + N'_D}. \qquad (17)$$

Into the rearranged relation (17) we introduced simultaneously the factor b, which expresses the influence of the defects on the changes of thermal conductivity.

For the irradiated samples, when $N'_D \gg N_{D0}$, the expression (17) has the form:

$$\lambda = \frac{R'_2}{b}\frac{T^{-z}}{N'_D}. \qquad (18)$$

The coefficients from the expression (17) or (18) have these numerical values: $R'_2 = 5.75 \times 10^{18}$ W cm^{-4}deg$^{0.8}$, $z = 1.8$.

In agreement with the experimental indications the factor b, which expresses the influence of radiation on the changes of thermal conductivity has the form:

$$\frac{1}{b} = 2^{\log 10 N_D'/N_{D_0}}. \tag{19}$$

Finally the expression for the thermal dependence of thermal conductivity of the irradiated samples has the form:

$$\lambda = R_2' \,.\, 2^{\log 10 N_D'/N_{D_0}} \times \frac{T^{-z}}{N_D'}. \tag{20}$$

The values of thermal conductivity $\lambda = f_\lambda'(T)$ calculated from the relation (20) are plotted in the graphs in Fig. 5 with dotted lines and the values $\lambda = f_\Phi(\Phi)$ for $T = 300$ °K are plotted in graphs in Fig. 8.

D. *The Z-parameter*

We get the dependence of the Z-parameter on the integral neutron flux, if we substitute the corresponding relations for the electrical conductivity (7), the Seebeck coefficient (13) and the thermal conductivity (20) into the expression for the Z-parameter. After the rearrangement we get the Z-parameter in the form:

$$Z = K_z \frac{k_n^{2\log \Phi/\Phi_0}}{2^{\log 10 N_D'/N_{D_0}}} \tag{21}$$

where the numerical value $K_z = 2.15 \times 10^{-18}\,\mathrm{deg}^{-1}$. The expression (21) is applicable for $N_D' > N_{D_0}$. The values $Z = f_Z'(T)$ and $Z = f_\Phi'(\Phi)$ are plotted in praphs in Fig. 6 and 7 with dotted lines.

CONCLUSION

The most important results which we obtained may be summed up as follows:

1. We have measured the negative changes of all parameters after the fast neutron irradiation.
2. The changes of the electrical conductivity and also of the Z-parameter are conspicuous at relatively small changes of the Seebeck coefficient and the thermal conductivity.
3. The change of the values of measured parameters begins only when $N_D' > N_{D_0}$ and ends when the integral neutron flux reaches the values of about $1 \times 10^{18}\,\mathrm{n'cm^{-2}}$.
4. We were successful in approximating experimental results with theoretical dependences, and the experimental and theoretical results are in a good agreement.*

REFERENCES

[1] Dismukes J. P., Elkstrom L., Steigmeier E. F., Kudman J., Beers D. S., J. Appl. Phys. *35* (1964), 2899.
[2] Krempaský J., Czech. J. Phys. *B 14* (1964), 533.
[3] Krempaský J., Čs. čas. fys. *A 16* (1966), 136.
[4] Kinchin G. H., Pease R. S., Rep. Prog. Phys. *18* (1955), 1.
[5] Macko P., Fyz. čas. SAV *17* (1967), 51.
[6] Smith R. A., *Semiconductors*. Cambridge 1959.

Received May 20th, 1969

Katedra fyziky
Elektrotechnickej fakulty SVŠT,
Bratislava

---

* I should like to express my gratitude to Prof. J. Krempaský for valuable suggestions and comments on my work and to Mr. P. Vybíral for assistance in experiments. I am very grateful to the other fellow workers from the Department of Physics of the Slovak Technical University for their help in assembling the experimental devices.