Vol. A40 (1971) ACTA PHYSICA POLONICA Fasc. 4

A STUDY OF THE DIFFUSION OF CHALCOGEN IMPURITIES IN SEMICONDUCTIVE II–VI COMPOUNDS

By J. Żmija

Military Academy of Technology, Warsaw*

(Received February 6, 1971)

The results of research on the diffusion of chalcogen elements in single crystals of semiconductive II–VI compounds (Se and Te in Cds, Se and Te in CdSe, and S and Se in CdTe) are presented. The diffusion processes were conducted from the gas phase under saturated vapour pressure of the diffusing impurity of the group VI component, or under condition of minimum overall pressure (Te in CdSe). Diffusion profiles were determined by means of the radioactive tracer sectioning technique based on measurements of the specific activity of the removed material and measurements of the intensity of radiation emitted by the sample after removal of each successive layer.

Diffusion profile analysis has shown that the diffusion flux of chalcogen elements in single crystals of semiconductive II–VI compounds resolves into two components, namely, into vacancy (slow) and interstitial (fast) diffusion.

A study of the diffusion as a function of temperature was made and on its basis it was found that the activation energy for the diffusion of chalcogen elements in the semiconductive II–VI compounds increases linearly with the square of the ionic radius of the diffusing element.

The performed experiments have shown that it is possible to prepare ternary compound of the type $A^{II}B^{VI}_{1-x}C^{VI}_x$ by the diffusion of chalcogen elements into semiconductive II–VI compounds.

1. *Introduction*

Research on the diffusion of chalcogen impurities in binary semiconductive II–VI compounds are undertaken for several reasons. One is that this technique provides a way of obtaining samples of ternary compounds, *e. g.*, of the $A^{II}B^{VI}_{1-x}C^{VI}_x$ type. Ternary compounds, on the other hand, are interesting because their properties can be altered appreciably by changing the composition. For example, the width of the energy gap in the CdS-Se system can be changed by changing the content of selenium substituted in the place of sulfur by diffusion. Another reason is that some of the $A^{II}B^{VI}_{1-x}C^{VI}_x$ compounds have been unachievable in single-crystalline form by the conventional synthesis of the compound components and their subsequent single-crystallization. For instance, the conventional method has proved unsuccessful in the aquisition of such ternary compounds as CdSTe

* Address: Wojskowa Akademia Techniczna, Warszawa 49, Poland.

and CdSeTe. Certain applications of these ternary compounds are expected. Moreover, interest is aroused by the effect of the content of the chalcogen element, which with cadmium forms compounds of the wurtzite structure (*e. g.*, S and Se) in single-crystalline samples of CdTe of sphalerite structure.

Attempts at solving this problem have been announced in the literature, but in the majority of cases these studies have a preliminary character. Handelman and Kaiser [1] have produced crystals of the ternary CdSSe compound by firing single-crystalline platelets of CdS 0.5 mm thick at 1050°C under an atmosphere of selenium. They determined the diffusion coefficient of selenium in CdS single crystals for these conditions from measurements of the absorption edge and for this temperature they obtained the value $D = 5\times10^{-9}$ cm²/sec. It should be kept in mind that this measurement was not performed under equilibrium conditions; notwithstanding, this result is in agreement with later radioisotopic measurements. Kato *et al.* [2] measured the diffusion of the radioactive isotope Se-75 in CdTe single crystals at an undetermined partial pressure of tellurium over the sample. The authors found that in the range of temperatures from 700 to 1000°C the change of the diffusion coefficients with temperature is expressed by the formula

$$D = 1.7\times10^{-4} \exp\left(\frac{-1.37 \text{ eV}}{kT}\right). \tag{1}$$

Woodbury and Hall [3] examined the diffusion of selenium in CdTe and CdS single crystals by radioisotopic techniques, employing the isotope Se-75. In single crystals of the first compound the diffusion of selenium was measured at a single temperature of 800°C, but under different pressures of selenium vapours; an inversely proportional dependence on partial pressure of cadmium vapours was found. On the other hand, investigations on the diffusion of selenium in CdS showed that there exists a slow and a fast component. The variation of these two types of diffusion components with temperature were found. These experiments were performed at 900°C under varying pressures of sulfur vapours (between 0.17 to 60 atm), which bear an effect on the diffusion profiles and the ratio of the participation of these two types of diffusion. Wherein these coefficients increase approximately proportionally to $P_S^{1/2}$.

In this work experiments concerned the diffusion of selenium and tellurium in CdS single crystals, sulfur and tellurium in CdSe single crystals, and sulfur and selenium in CdTe single crystals. Investigations were carried out by the radioactive tracer techniques employing the radioisotopes S-35, Se-75 and radioisotopic mixture containing Te-123 *m*, Te-127 *m* and Te-129 *m*.

2. *Experimental*

The single crystals of cadmium sulfide used in these experiments were obtained by a modified Piper and Polish technique, whereas the cadmium selenide and cadmium telluride crystals were breeded by the vertical Bridgman method from the liquid phase [4]. The single crystals chosen for study were oriented by the X-ray technique and 5×5×2.5 mm samples were cut from them; the larger surfaces were (0001) planes or planes perpendicular

to it (usually $(11\bar{2}0)$), and in the case of CdTe the surfaces were (110) planes. The single crystals used in this work had a dislocation density of the order of 10^3 to 10^4 cm^{-2}. This was determined by X-ray and etch pit methods [4]. The surfaces of all samples were mechanically ground and polished, and in order to remove structure deformations due to mechanical working they were briefly polished chemically in the following solutions: 1) for CdS concentrated HCl at room temperature; 2) for CdSe a solution containing three parts of concentrated HCl and two parts of a saturated solution consisting of seven parts K_2CrO_3 per three parts of concentrated sulfuric acid; and 3) for CdTe a solution similar to that for CdSe but without the muriatic acid [5].

The diffusion processes were conducted from the gas phase. Samples with weighed portions of the atmosphere components and radioisotopes were sealed under vacuum (of the order of 10^{-5} torr) in quartz ampoules.

The firing was accomplished in wire-wound joule heating furnaces in which a stabilization of temperature to within = 10°C was obtained due to the thermal equilibrium of the system. The temperature and its distribution were determined with a thermocouple connected up with an indicator, compensator or thermoregulator. After the ampoules were extracted from the furnace they and their contents were quickly cooled in water. To eliminate any perturbing effects of surface diffusion on the measurements, a layer greater in thickness than the presumed diffusion range (500 μm) was removed off all surfaces of the samples except that surface which was to be employed in the investigation. The samples prepared in this way were analyzed by the radioactive tracer sectioning method. In the case when the sectioning analysis was based on measurements of radiation intensity after the removal of each successive layer, these layers were subtracted by mechanical abrasion on No 400 water-proof abrasive paper. On the other hand, when the specific activities of the removed layers were measured, then apart of this the layers were also removed by chemical polishing in the above-mentioned solutions.

Measurements of gamma radiation intensity after the removal of a successive layer off the sample were made with GAH Geiger-Müller counters and a scintillation counter. The specific activities of the polishing solutions were measured with a liquid counter manufactured by Vakutronik (GDR). A PEL-5 scaler was used for counting the counter pulses. All diffusion processes were performed under conditions of pressure of the diffusing component's saturated vapour or that of the compound component into which the diffusion process occurs, or yet under conditions of minimum overall pressure (Te in CdSe).

To calculate the diffusion coefficients of selenium and tellurium in CdS, tellurium in CdSe, and selenium in CdTe from the shape of the profiles found from specific activity measurements of the removed layers use was made of the expression

$$i(x_n, t) = \frac{\text{const}}{\sqrt{\pi D t}} \exp\left(\frac{-x_n^2}{4Dt}\right) \tag{2}$$

where $i(x_n, t)$ is the specific activity of layers at depth x_n after time t of firing under constant temperature, and D is the diffusion coefficient.

In all experiments on the diffusion of sulfur performed in this work, when the diffusion profiles were determined *via* measurement of the intensity of soft beta radiation, the diffusion

coefficients were calculated from the expression

$$I_n = \frac{\text{const}}{\sqrt{\pi D t}} \exp\left(-\frac{X_n^2}{4Dt}\right). \tag{3}$$

Here, I_n is the intensity of radiation after a layer of thickness X_n is removed from the sample, and the other notation is the same as that used in Eq. (2).

Both of the above expressions are solutions of the second Fick law for the corresponding experimental conditions [6].

The temperature changes of the diffusion coefficients were approximated to the known Arrhenius formula

$$D = D_0 \exp\left(\frac{-E}{RT}\right) \tag{4}$$

where D_0 is the frequency factor, R the gas constant, E the activation energy and T absolute temperature.

The diffusion coefficients were calculated from the experimental data with the help of Eqs (2) and (3), and the activation energy with Eq. (4), while the errors with which these quantities are burdened were found by the least squares method on a computer. The estimated error of diffusion coefficient determination is not more than 20 per cent, the frequency factor 45 per cent, and activation energy 5 per cent.

3. Diffusion of selenium and tellurium in CdS single crystals

The diffusion penetration profiles in CdS single crystals were found by the radioisotope tracer analysis using the isotope Se-75 based on specific activity measurements of the removed layers. Since earlier studies had provided a lot of information on the vacancy and interstitial diffusion of Se in CdS [3] and their changes with the temperature of diffusive firing under saturated sulfur vapour pressure, the present studies were performed under conditions of saturated selenium vapour pressure.

Figure 1 presents a typical diffusion profile, in which it is seen that the diffusion flux consists of two components, namely, vacancy (slow) diffusion and interstitial (fast) diffusion. The temperature dependence of the coefficients of these two types of diffusion is shown in Fig. 2. The straight lines shown here may be described by the following equations: for interchange diffusion

$$D = 6.1 \times 10^{-2} \exp\left(\frac{-44400}{RT}\right) \tag{5}$$

and for interstitial diffusion

$$R = 1.2 \exp\left(\frac{-44000}{RT}\right). \tag{6}$$

The differences between the vacancy and interstitial diffusion coefficients of selenium in CdS single crystals at a fixed temperature reach two orders of magnitude, whereas their

activation energies are comparable. This last finding is rather unexpected. The decrease of the difference in activation energy of these two types of diffusion, as compared with the same difference observed in the self-diffusion of sulfur in CdS, may be explained by the larger ionic and valence radii of selenium relative to the corresponding dimensions of sulfur ions.

No experiments have been made on the effect of partial selenium pressure on the selenium diffusion rate. This is so because on the basis on the above-presented results of investigations on the self-diffusion of chalcogen elements in single crystals of semiconductive II–VI compounds and results of studies on the diffusion of selenium in CdS single crystals at

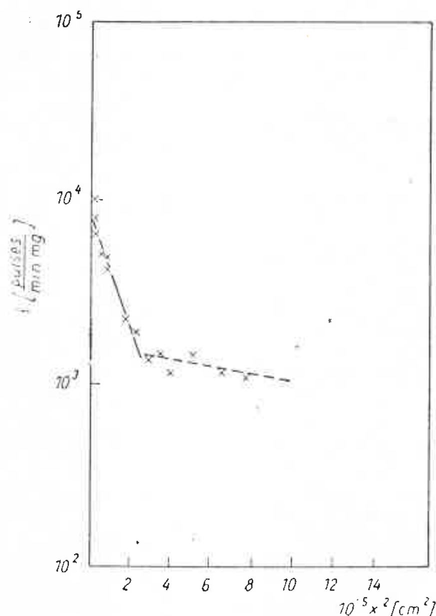

Fig. 1

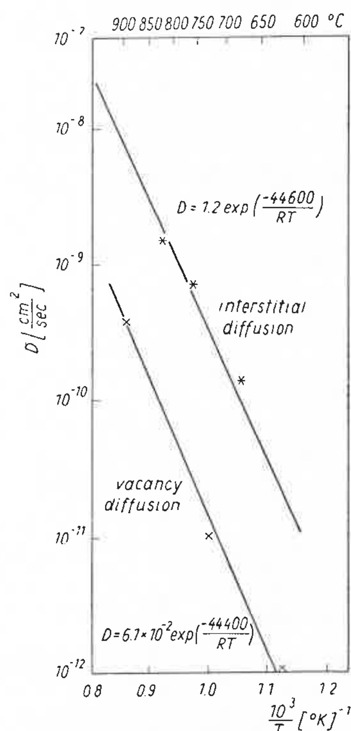

Fig. 2

Fig. 1. Diffusion profile of selenium in CdS single crystals along [0001] direction under saturated selenium vapour pressure at 900°C for 5 hrs

Fig. 2. Temperature dependence of the coefficients of vacancy and interstitial diffusion of selenium in CdS single crystals along [0001] direction under saturated selenium vapour pressure

saturated sulfur vapour pressure, presented in Ref. [3], it should be expected that the values of the selenium diffusion coefficients will increase proportionally to the square root of its vapour's pressure.

In the investigations on the diffusion of tellurium in CdS single crystals use was made of the radioactive tracer sectioning technique based on measurements of the specific activity of the removed layers. Diffusion was accomplished exclusively under conditions of saturated sulfur vapour pressure. The diffusion profiles obtained were similar

to that presented in Fig. 1. The temperature dependence of the interchange and interstitial diffusion coefficients obtained from these profiles and presented in Fig. 3 may be expressed by means of the following equations:
for vacancy diffusion

$$D = 0.13 \exp\left(\frac{-51800}{RT}\right) \tag{7}$$

and for interstitial diffusion

$$D = 3.62 \times 10^{-2} \exp\left(\frac{-43000}{RT}\right). \tag{8}$$

In this case attention should be turned at the low values of the coefficients of diffusion of tellurium as compared with the respective coefficients of selenium diffusion and sulfur self-diffusion in CdS single crystals. The main cause for this is the large valence and ionic

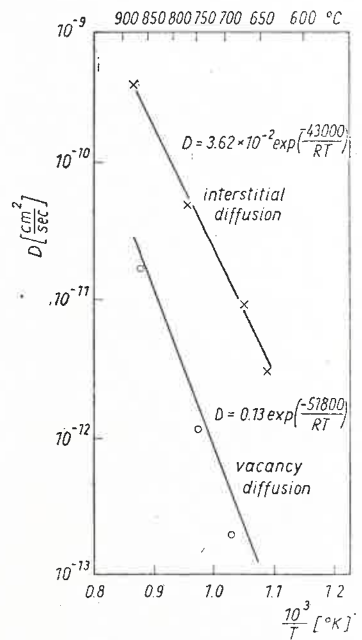

Fig. 3. Temperature dependences of the coefficients of fast and slow diffusion of tellurium in CdS single crystals along [0001] direction under saturated sulfur vapour pressure

radii of tellurium taken relative to the respective radii for sulfur and the tendency of tellurium to form other structures and its low solubility in CdS [7]. The large values of activation energy for both types of diffusion should be explained on similar grounds. As opposed to the case of diffusion of selenium in CdS, in this case once again there is observed a proper difference between the activation energies for the vacancy and interstitial types of diffusion.

4. *Diffusion of sulfur and tellurium in CdSe single crystals*

Studies on the diffusion of sulfur in single crystals of CdSe were performed by the radioactive tracer sectioning technique basing on measurements of radiation intensity after the removal of successive layers. This technique was also employed in investigations on the diffusion of tellurium in the same single crystals, but specific activity measurements of the removed layers constituted the basis. The diffusion of sulfur and tellurium was conducted under conditions of saturated selenium vapour pressure and, in addition, tellurium diffusion under minimum overall pressure. The inflections in the diffusion profiles were sometimes found to appear irregularly. Therefore, in general considerations only vacancy diffusion was taken into account.

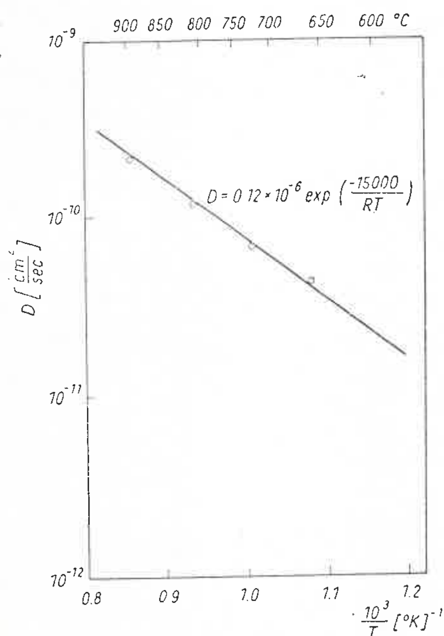

Fig. 4

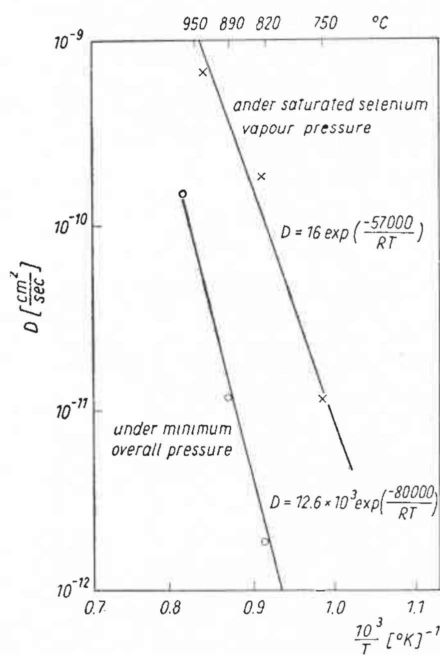

Fig. 5

Fig. 4. Temperature dependence of coefficients of vacancy diffusion of sulfur in CdS single crystals along [0001] direction under saturated selenium vapour pressure

Fig. 5. Temperature dependence of coefficients of diffusion of tellurium in CdSe single crystals along [0001] direction

The temperature dependence of the coefficients of vacancy diffusion of sulfur in CdSe single crystals is presented in Fig. 4, the curve being described by the equation

$$D = 0.12 \times 10^{-6} \exp\left(\frac{-15000}{RT}\right). \tag{9}$$

On the other hand, Fig. 5 gives the temperature dependence of the vacancy diffusion of tellurium for the corresponding conditions.

These curves may be described by means of the equations:
for diffusion at saturated selenium vapour pressure

$$D = 16 \exp\left(\frac{-57000}{RT}\right). \tag{10}$$

and for diffusion under conditions of minimum overall pressure

$$D = 12.6\times 10^3 \exp\left(\frac{-80000}{RT}\right). \tag{11}$$

As in the case of the diffusion of selenium and tellurium in CdS single crystals, geometrical factors bear a decisive effect on the values of both the diffusion coefficients and activation energies. The pronouncedly lower values of activation energy of tellerium diffusion in CdSe single crystals compared with that of this element in CdS single crystals is explainable by the lower value of lattice constant of the former compound relative to the latter, and also by the lower solubility of tellurium in CdSe and its tendency to form other structures. The results shown in Fig. 5 imply that in this case also the diffusion coefficients increase with higher pressures of the chalcogen element vapours under which the diffusion processes are being conducted.

5. *Diffusion of sulfur and selenium in CdTe single crystals*

Sulfur and selenium diffusion in CdTe single crystals was examined by the same methods as described above (*cf.* diffusion of sulfur in CdSe and selenium in CdS). The diffusion profiles in this case also did not show any irregular participation of the two types

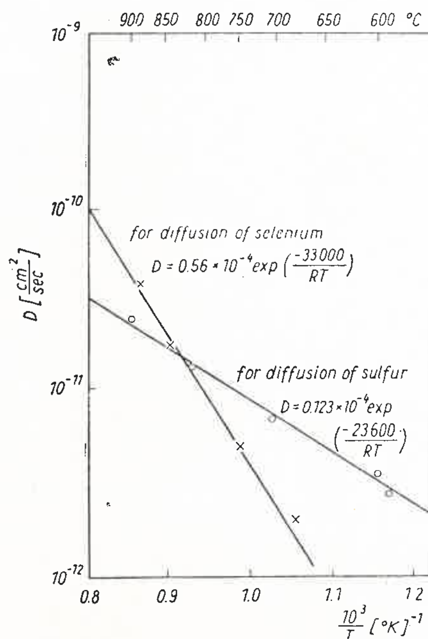

Fig. 6. Temperature dependence of the vacancy diffusion of sulfur in CdTe single crystals along [110] direction under saturated selenium vapour pressure

(interchange and interstitial) of diffusion. Hence, only the coefficients of the first kind of diffusion were regarded. The temperature dependences of the corresponding diffusion coefficients are presented in Fig. 6, and they may be described by the following equations: for the diffusion of sulfur in CdTe

$$D = 1.2 \times 10^{-5} \exp\left(\frac{-23600}{RT}\right) \tag{12}$$

and the diffusion of selenium in CdTe

$$D = 0.56 \times 10^{-4} \left(\frac{-33000}{RT}\right). \tag{13}$$

This last dependence is approximately in conformity with that found by Kato and collaborators [2]. However, they did not define the partial pressure under which the investigations of selenium diffusion in CdTe single crystals were carried out. As earlier, these dependences may be explained by taking into account dimensional factors, *i. e.* the radii of the diffusing atoms and the lattice constants of the matrix into which diffusion atoms penetrate. The tendency to form a different structure by the diffusing element bears in this case an opposite effect, that is, it decreases the diffusion activation energy.

6. *Discussion of results*

It is seen from the obtained results that in the diffusion of chalcogen elements in semiconductive II–VI compounds the same regularities appears as in the self-diffusion of chalcogen elements in these compounds. Diffusion here has a vacancy-interstitial character,

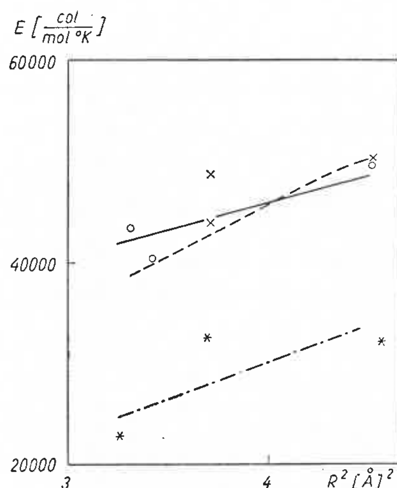

Fig. 7. Dependence of activation energy of vacancy diffusion in semiconductive II–VI compound single crystals under maximum chalcogen pressure chonditions upon the square of the atomic radius of the diffusing element [7]. O — vacancy diffusion in CdS single crystals, × — vacancy diffusion in CdSe single crystals, * — vacancy diffusion in CdTe single crystals

hence, it possesses a slow diffusion component and a fast one. Their relative share in the effective diffusion flux depends on the conditions under which this process is conducted (temperature, composition and partial pressure of the individual constituents in the vapour above the fired sample, and so on) and on the type of the compound and diffusing element. Together with an increase in the partial pressure of the chalcogen element there are increases in the values of the interchange diffusion coefficients.

As in the case of self-diffusion of the chalcogen elements [4, 8] this may be explained by two phenomena. The first is that under the pressure of the chalcogen element the stoichiometry of the pure II–VI single crystals becomes changed due to a drop in the concentration of the VI constituent vacancies and a rise in the cadmium vacancies. The other is that there exist processes of equilibrium transitions of the diffusing atoms and interstitial sites to crystal lattice points.

In investigations on the diffusion of chalcogen impurities in semiconductive II–VI compounds it was found that the dimensional factor bears some influence on the progress of the diffusion. In Ref. [7] it was ascertained that the activation energy of the diffusion of impurities in pure metals increases linearly with an increase of the square of the ionic radius of the impurity. Graphs of such dependences for the diffusion of chalcogen impurities in II–VI compounds under pressure of the saturated vapour of the chalcogen element (Fig. 7) were plotted and it was found that in this case this law is, in principle, valid here also.

Chalcogen impurities in semiconductive II–VI compounds can give rise to donor and acceptor levels alike. This may be explained only on the basis of the difference in their ionic radii relative to the ionic radii of the chalcogen elements in the matrix. Very low values of diffusion coefficient were obtained for the diffusion of tellurium in CdS and CdSe single crystals and sulfur and selenium in CdTe single crystals. This is due to the low solubility of the diffusing impurity in the matrix. A similar phenomenon was revealed during a study on the diffusion of tin, antimony and iron in aluminum [7]. As in the case of the diffusion of iron in aluminum, there was found here a large (accelerating) effect of dislocations of semiconductive $A^{II}B^{VI}_{x}C^{VI}_{1-x}$ compounds.

The results of these investigations imply that it should be possible to utilize the diffusion of chalcogen impurities into binary semiconductive II–IV compounds in the production of semiconductive compounds of the $A^{II}B^{VI}_{x}C^{VI}_{1-x}$ type. This is particularly important when unsurmountable difficulties are encountered in the procurement of the ternary compound by means of the process of synthesis and single-crystallization.

REFERENCES

[1] E. T. Handelman, W. Kaiser, *J. Appl. Phys.*, **35**, 3519 (1964).
[2] H. Kato, M. Yokozawa, S. Takayanagi, *Japan J. Appl. Phys.*, **4**, 1019 (1965).
[3] H. H. Woodbury, R. B. Hall, *Phys. Rev.*, **157**, 641 (1967).
[4] J. Żmija, *Biul. WAT*, **2**, 210 (1970) (in Polish).
[5] *Travlenie poluprovodnikov*, PTJ, ed. Moskva 1969.
[6] J. Żmija, *Radioizotopowe badania dyfuzji w metalach*, PTJ, Warszawa 1967 (in Polish).
[7] J. Żmija, *Biul. WAT*, 65, **13**, (144) 8 (1964) (in Polish).
[8] J. Żmija, M. Demianiuk, *Biul. WAT*, 77, **19**, (217) 9 (1970) (in Polish).