Vol. A43 (1973) ACTA PHYSICA POLONICA No 3

INVESTIGATION OF SELF-DIFFUSION OF CADMIUM AND SELENIUM IN CdSe SINGLE CRYSTALS

BY J. ŻMIJA

Military Academy of Technology, Warsaw*

(Received January 20, 1972; Revised paper received March 29, 1972)

Investigation of self-diffusion of Cd and Se in CdSe single crystals have been carried out by means of radioisotope tracer section method. The self-diffussion process was studied in sealed amploules in the vapours of the investigated elements atmosphere under different pressures. It was found that the diffussion profiles are the result of two processes: one slow (interchange mechanism) and the other fast (interstitial mechanism). The contributions of these two mechanisms depend on the temperature, and partial pressure of the element as well as the impurity concentration contents in the sample. The results are explained in terms of native and impurity point defects in II–VI semiconducting compounds.

1. Introduction

There is much experimental evidence that native point defects strongly influence the electrical and optical properties of II–VI semiconducting compounds, however, the present knowledge of detailed features of this problem is insufficient. The high temperature equilibrium of defects in pure single crystals is usually studied by heating the sample to high temperatue, "freezing" by rapid cooling to low temperature and subsequent measurement of the electrical and optical properties of the crystals. There is some evidence [1], however, that during rapid cooling to low temperature, the high-temperature equilibrium state is not maintained and thus the measurements of the electrical and optical properties after this procedure, do not represent the high temperature equilibrium state.

Investigation of the equilibrium states of point defects in II–VI semiconducting compounds can be carried out by means of radiometric measurements of self-diffusion of their radioisotope components. These studies consist in the determination of the self-diffusion profile at high temperature, subsequent rapid cooling and determination of the profiles of the radioisotope concentration changes in the sample, at room temperature.

* Address: WAT, 00-908 Warszawa, Poland.

The present paper gives the results of radioisotope tracer studies of the self-diffusion of cadmium and selenium in CdSe single crystals. The results concerning the self-diffusion of sulphur and cadmium in CdS crystals have been published earlier [2].

The results obtained are the basis for the discussion of problems connected with point defects in II–VI semiconducting compounds.

2. *Experimental*

The CdSe single crystals obtained by a method described in Refs [3, 4] were oriented by means of the *X*-ray method. A diamond saw was used to cut out oriented $5 \times 5 \times 2.5 cm^3$ plates whose greater square faces were the (0001) planes. All samples were polished mechanically. To remove distortion of the crystals structure produced during mechanical treatment the samples were also subject to chemical polishing for a short time. The diffusion process was carried out from gaseous phase. The samples and weighted portions of suitable radioisotopes in the vapour of which the diffusion was carried out were located together in sealed ampoules. Before loading, the ampoules were carefully washed in *aqua-regia*, in highly concentrated HNO_3 and deionized water, and then dried.

The size of weighted portions of components in the vapour which the diffusion process occurred was determined taking into account the model of varying diffusion source and the vapour pressure under which the particular diffusion experiment was made. This vapour pressure defines not only the diffusion rate but also the mechanism of the diffusion processes.

Filled quartz ampoules were evacuated to about $10^{-4}-10^{-5}$ Tr and then cut off from the vacuum pump. Next the samples were annealed in one- and two-zone resistance furnaces in which the annealing temperature was stabilized within $\pm 5°C$ keeping the heating system in thermal equilibrium. The distribution of the temperature along the furnace was measured, using Pt-PtRh thermocouples connected to a recorder or thermostatic control system.

After removing from the furnace, the ampoules were rapidly cooled in water. In order to eliminate the influence of surface diffusion, sections of thickness greater than the probable diffusion range (100–500 μm) were taken off from all surfaces except this one used for the measurements. The samples prepared in this way were investigated by the method of the radioisotope tracer analysis.

The investigated layers were ground off by mechanical polishing using 4/0 emery paper in convenient holders to guarantee the parallellness of layers. They were also removed by means of chemical polishing using a solution which contained 3 parts of concentrated HCl and 2 parts of saturated solution 7 parts of K_2CrO_3, and 3 parts of concentrated H_2SO_4.

The depth of the sections was measured basing on the decrease in weight after removing a subsequent section by means of a semiautomatic balance with the accuracy of 10^{-5} g. It was also measured on samples by means of Abbe comparator.

The measurements of the gamma or beta radiation intensity emitted by the sample after removing subsequent section or measurement of the specific activity of this section

were carried out by means of GM-counters (type GAH ane BAH) and also by means of a scintillation counter connected to a PEL–5 scalar. The obtained result was elaborated using the least squares method. The errors of the diffusion coefficients determined did not exceed 5%.

3. Experimental results

3.1. Self-diffusion of selenium

Investigations of the self-diffusion of selenium were carried out using the ^{75}Se radioisotope obtained by activation of specpure natural selenium with slow neutrons in the EWA-reactor at Świerk after suitable cooling down period. The half-life of this radioisotope is $T_{1/2} = 127$ days. The decay scheme is rather complex [5] and the emitted radiation is mainly gamma type with energies ranging from 0.666–0.405 MeV. The analysis was mainly based on measurements of the specific activity of the sections. The profile in Fig. 1

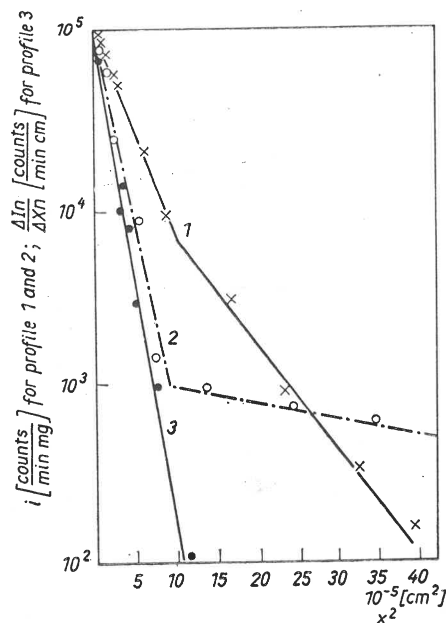

Fig. 1. Self-diffussion profiles for Se and Cd in CdSe single crystals. *1* – self-diffusion of selenium at 820°C during 20 hours under the pressure of saturated Se vapour; *2* – self-diffusion of selenium at the same time, but under the pressure of 0.1 of that of saturated vapour; *3* – self-diffusion of cadmium at 700°C during 7 hours under saturated cadmium vapour pressure

is a typical profile of the self-diffusion of selenium in CdSe single crystals annealed in saturated selenium vapour ($p_{Cd} = 2.2 \times 10^{-6}$ atm) for 20 hours at 820°C. In such conditions the diffusion profile exhibits a small bend not too distinct however, when for the same annealing temperature the same time and pressure equal to 0.1% of the saturated selenium vapour pressure this bend is considerable (see profile No 2 in Fig. 1). When the self-diffusion of selenium was carried out at 890°C for 25 hours under the pressure

$p_{Cd} = 0.22$ atm the self-diffusion profile is almost a straight line as it can be seen in Fig. 2 (profile No 2). However, in the same condition of time and temperature, but under higher pressure ($p_{Cd} = 0.8$ atm) the profile is no more a straight line (profile No 1 in Fig. 2). Since the occurrence of bends in the profiles does not exhibit any regularity, the present analysis

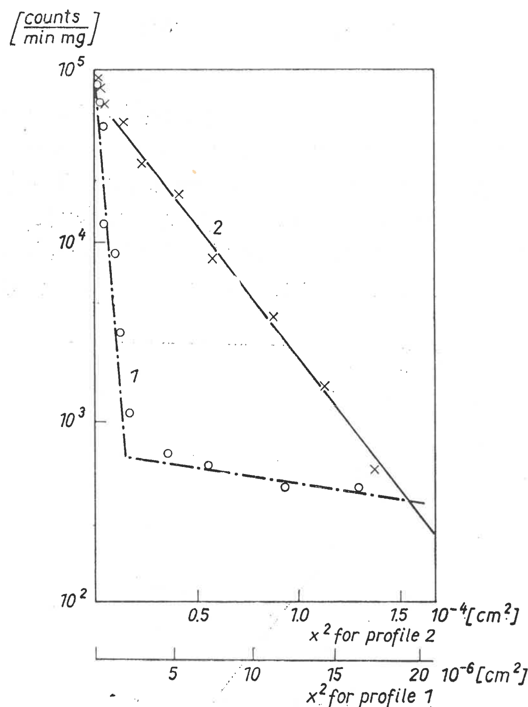

Fig. 2. Self-diffusion profiles in CdSe single crystals obtained at 890°C during 25 hours. *1* – under Cd-vapour pressure of 0.8 atm; *2* — under Cd-vapour pressure of 0.22 atm

is concerned only with the parts of the profiles under the bend, similarly to the curves without bends which are characteristic for slow (interchange diffusion) as it has been shown in Refs [2, 3] and below.

The self-diffusion coefficients were calculated using the expression from Ref. [7]

$$i(x, t) = \frac{\text{const}}{\sqrt{\pi D t}} \exp\left(\frac{-x^2}{4Dt}\right) \tag{1}$$

where $i(x, t)$ is the specific activity of the section at a given depth x after annealing for the time t, and D is the diffusion coefficient.

All the results obtained from investigations of the influence of temperature and cadmium vapour partial pressure above the annealed sample are summarized in Fig. 3. It can be seen from this figure that the coefficients of interchange self-diffusion of selenium are inversely proportional to the partial pressure of cadmium vapour:

$$D_{Se} = K_T p_{Cd}^{-1}. \tag{2}$$

The values of K_T calculated from the dependences of the self-diffusion coefficients on pressure shown in Fig. 3 are plotted in Fig. 4 in $\log K_T$ *vs* $\frac{1}{T}$ terms. The calculated points

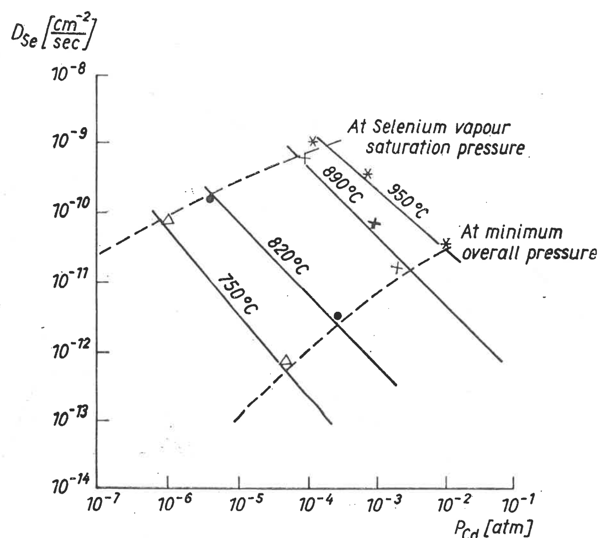

Fig. 3. Dependence of the self-diffussion coefficient of Se in CdSe single crystals on Cd vapour pressure

on a straight line whose equation has been determined in accordance with (2) by means of the least squares method with the help of a computer. This equation is as following

$$K_T = 2 \cdot 10^5 \exp\left(\frac{-101200}{RT}\right). \tag{3}$$

The temperature dependence of the self-diffusion coefficients for the two most interesting extreme cases, *i. e.* for minimum value of pressure ($p_{Cd} = 2p_{Se}$) and the pressure of saturated vapour of selenium, are shown in Fig 5. They were approximated by the well-known relationship of Arrhenius

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

where D is the self-diffusion coefficient, D_0 is the frequency coefficient, E — the activation energy, T — the temperature and R — the gas constant.

These dependences can be described by the following equations: for the diffusion process occurring under minimum total pressure (curve *2*)

$$D_{Se} = 9.04 \cdot 10^{-3} \exp\left(\frac{-49800}{RT}\right) \tag{5}$$

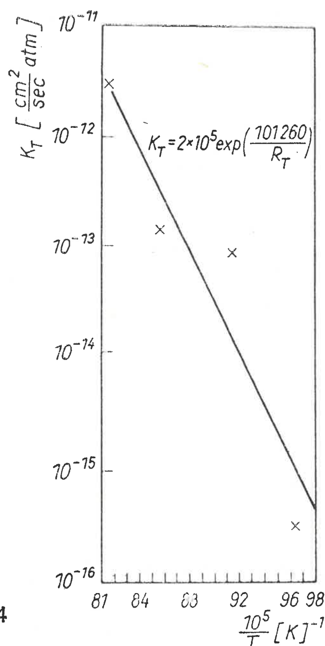

Fig. 4

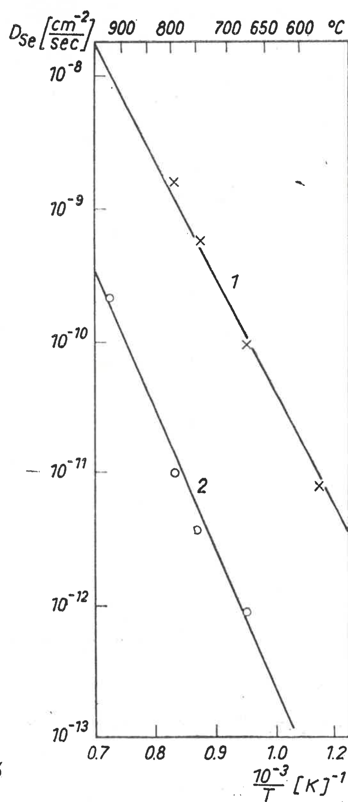

Fig. 5

Fig. 4. K_T for interchange slow diffusion of selenium in CdSe single crystals in the direction [0001]. *vs* $1/T$

Fig. 5. Temperature dependence of self-diffusion coefficients of Se in CdSe single crystals in the direction [0001]. *1* – under saturated vapour pressure of Se; *2* – under minimum total pressure

TABLE I

Self-diffusion constants of Se and Cd in pure and indium doped CdSe single crystals

	Selenium		Cadmium		
	Under minimum total pressure	Under the pressure of saturated selenium vapour	Under the pressure of saturated selenium vapour	Under the pressure of saturated cadmium vapour	
$D_0 \frac{cm^2}{sek}$	$9.04 \cdot 10^{-3}$	$8.83 \cdot 10^{-3}$	$4.12 \cdot 10^{-2}$	$6.3 \cdot 10^{-2}$	$1 \cdot 10^{-5}$
$E \frac{cal}{g.atom}$	49800	38600	50000	38600	19100
	Pure samples				Samples doped with indium to 10^{18} atoms/cm^3

and for the diffusion occurring under the pressure of saturated selenium vapour pressure (curve *1*):

$$D_{Se} = 8.83 \cdot 10^{-3} \exp\left(\frac{-38600}{RT}\right). \tag{6}$$

The self-diffusion constants appearing in these formulas have been also summarized in Table I.

3.2. Self-diffusion of cadmium

The investigations of the self-diffusion of cadmium in CdSe single crystals were carried out using the ^{115}Cd radioisotope which was obtained by irradiation of specpure cadmium in the EWA-reactor at Świerk with slow neutrons (neutron flux of about 10^{13}). The irradiation time was 100 hours and the subsequent cooling-down period of six days.

Cadmium-115 is both a beta and gamma emitter with the half-life $T_{1/2} = 43$ days. The gamma spectrum consists of a number of lines in the range 0.337–1.280 MeV with the predominance of the more energetic part.

The studies of the self-diffusion of cadmium in pure CdSe single crystals in the direction [001] were carried out under different partial pressures of cadmium, mainly under the pressure of saturated vapour of cadmium and selenium. Such studies were also carried out on samples doped by copper, however, only under the pressure of saturated cadmium vapour. The diffusion profiles were obtained by measurement of the specific activity of the removed sections and by measurement of the intensity of radiation of the sample after remowing subsequent section. In the former case the diffusion coefficients were calculated using Eq. (1), while in the latter the formula used was:

$$\frac{\Delta I_n}{\Delta x_n} = \frac{\text{const}}{\sqrt{\pi D t}} \exp\left(\frac{-x_n^2}{4Dt}\right) \tag{7}$$

which is the solution of the Fick equation in these conditions and the denotations are the same as in Eq. (1) except ΔI_n which denotes the change in the intensity of radiation after removing a consecutive section of the thickness Δx_n. These profiles did not exhibit any distinct bend (profile No 3 in Fig. 1) which is characteristic for the case when the diffusion flux consists of both the slow and the fast components. Fig. 6 shows the changes in the self-diffusion vapour pressure of cadmium (curve *2*) and selenium (curve *1*). Both relationships concern the self-diffusion in pure CdSe single crystals.

The curves presented in the figure were approximated by the Arrhenius equation (Fig. 4) and have the following forms: for the self-diffusion occurring under the pressure of saturated vapour of cadmium (curve *1*):

$$D_{Cd} = 6.3 \cdot 10^{-2} \exp\left(\frac{-38600}{RT}\right) \tag{8}$$

and for the self-diffusion under the selenium vapour pressure (curve *1*):

$$D_{Cd} = 4.12 \cdot 10^{-2} \exp\left(\frac{-50000}{RT}\right). \tag{9}$$

The constants appearing in Eqs (8) and (9) are also summarized in Table 1. The temperature changes in the self-diffusion coefficients of cadmium in CdSe single crystals doped by indium (10^{18} atoms/cm^3) are presented by the broken line (*3*) in Fig. 6. Before the

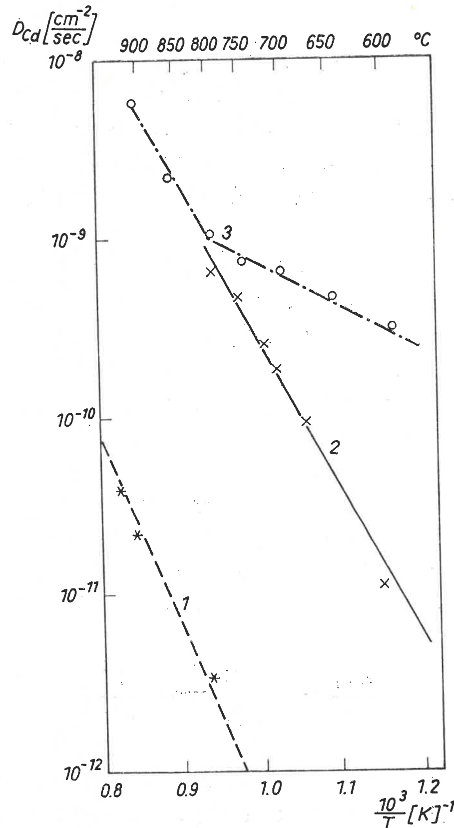

Fig. 6. Temperature dependence of the interchange self-diffusion coefficient for Cd in CdSe single crystals in the [0001] direction. *1* – for self-diffusion under saturated vapour pressure of Se in pure samples; *2* – for self-diffusion under saturated vapour pressure of Cd in pure samples; *3* – for self-diffusion under saturated vapour pressure of Cd in indium-doped samples (10^{18} at/cm^3)

bending point the line coincides with extrapolated straight line (*2*) (upper line) while the part of the line after bending can be described by the equation

$$D_{Cd} = 1.0 \cdot 10^{-5} \exp\left(\frac{-19100}{RT}\right). \tag{10}$$

For the sake of comparison the self-diffusion constants occurring in this equation have been listed in the last column of Table I.

4. *Discussion of the results and conclusions*

The results of the investigations of the self-diffusion of cadmium and selenium in CdSe single crystals obtained in the present work as well as those published in earlier papers [2, 3] indicate that the self-diffusion of the elements of the oxygen family occurs by two mechanisms: the interchange (slow) and interstitial mechanisms. Occurring or not this latter process, depends on the temperature and on the partial pressure of the particular elements participating in the diffusion process. It was found that interstitial diffusion becomes more important the higher the temperature and the lower the partial pressures (*cf.* Fig. 5 and Eq. (2)). On the other hand it has been also shown that the rate of exchange -diffusion increases with increasing partial pressure. This proportionality between the self-diffusion coefficients and cadmium vapour pressure is not observed if the cadmium pressure is maximum. The last fact is clearly seen particularly in the case of self-diffusion of sulphur in CdS single crystals [2]. In this case the mechanism of self-diffusion will be probably different. It seems that in the whole investigated partial pressure range the dominant mechanism is exchange-vacancy diffusion. It is not possible however to explain the inverse-proportionality between the self-diffusion coefficients and cadmium vapour pressure in the framework of this mechanism, since according to the simple model of point defects the concentration of vacancies remaining after the atoms of the oxygen family as well as the coefficients of their self-diffusion should increase together with increasing partial pressure of cadmium vapour.

From the comparison of the activation energies of exchange self-diffusion of selenium in CdSe single crystals (Eqs (5) and (6) and Table I) it follows that the activation energy in the process under minimum overall pressure is greater than in case when the selenium vapour is saturated. This is probably connected with the fact that under smaller selenium pressures the concentrations of vacancies remaining after selenium atoms are greater as well as the probability of the formation of divacancies which are characterized by smaller migration energies.

The self-diffusion of selenium into CdSe single crystals which occurs under saturated selenium vapour pressure is accompanied by a decrease in the concentration of interstitial position of cadmium, similarly as it was observed in the case of the self-diffusion of sulphur in CdS single crystals [2, 3]. This decrease is the main reason for the decrease in the resistivity of the sample in the region where the self-diffusion occurs. The change in the physical and electrical properties of II–VI semiconducting compounds in particular the change of resistivity is now explained on the basis of the model of point defects. During the annealing of such samples in the atmosphere of the oxygen group elements, cadmium vacancies are produced, which in this case are acceptors and by compensation, increase the resistivity while the interstitial positions of oxygen group atoms do not play any active role as far as the electrical properties are concerned [12]. The validity of such explanation is supported by the fact which has been found in the first, preliminary stage of investigations, namely, that the self-diffusion of oxygen family atoms in interstitial positions of the structure of II–VI compounds does not depend on doping. This fact suggests that the defects participating in this process are electrically neutral.

The inverse proportional dependence of the interstitial self-diffusion of sulphur in CdS and selenium in CdSe on partial pressure of cadmium can be explained, if one assumes that local equilibrium is established between the rapidly diffusing atoms in interstitial positions and the atoms in the sites of the crystal lattice of II–VI semiconducting compounds. An important role in self-diffusion processes is thus played by the exchange reaction between these two types of point defects [8].

On the basis of the accepted model of interstitial-exchange self-diffusion and the present measurement results it is possible to estimate the approximate values of concentrations of point defects introduced into the lattice. It follows from the results of the study of selenium self-diffusion into CdSe carried out at 900°C that the concentrations of point defects are as following: for the maximum selenium pressure $[Se_i] = i \times 10^{-4}$ of molar fraction ($C = 2 \times 10^{18}$ cm^{-3}), while for the maximum cadmium pressure $[Cd_{Se}] = 10^{-7}$ of molar fraction ($C = 1.5 \times 10^{15}$ cm^{-3}). It is seen that the concentration of vacancies is comparable or smaller than the maximum possible residual concentration of cadmium in the present technology.

The temperature changes in the self-diffusion coefficients of cadmium in pure CdSe single crystals which are shown in Fig. 6 (profiles *1* and *2*) and which are described by Eqs (8) and (9), as well as the self-diffusion constants appearing in these equations and listed in Table I, have a similar character as in the self-diffusion of cadmium in CdS single crystals [2, 3]. There is no reason to believe that their interpretation should be different. The basis of the model which explains the results obtained is again the model of interstitial-interchange diffusion and the interchange of the type interstitial-lattice sites. This mechanism may be the basis for the explanation of rapid changes in the electric properties of CdSe single crystals observed after their thermal diffusion treatment. In this case, however, one should bear in mind that there is also diffusion along the dislocations.

The results obtained from investigations of self-diffusion of cadmium are described by the broken line (*3*) in Fig. 6, Eq. (10) and the self-diffusion constants are given in the last column of Table I. In the framework of the model of interchange and interstitial mechanism the following explanation can be given. At lower temperatures when the concentrations of cadmium vacancies are smaller than those of ionized donor impurities the influence of the latter will be displayed in the increase in the concentration of ionized cadmium vacancies and in the increase of cadmium self-diffusion coefficients. At high temperatures, when the concentration of cadmium vacancies is greater than that of donor impurities, the self-diffusion process is independent on the concentration of donor impurities. This fact is confirmed by the shape of the curve *3* in Fig. 6 below its bend and by the shape of the straight curve *2* in the same figure. Assuming that the self-diffusion of cadmium in CdSe single crystals doped with indium occurs as a result of the displacement of ionized cydmium vacancies and as a result of the fact that the concentration of these vacancies is comparable with the concentration of donor impurities, the activation energy determined from the slope of the line above the bend (E = 19.100 cal/mole) represents the activation energy of the motion of ionized cadmium vacancies. The measurement of the self-diffusion of cadmium made at 800°C on a CdSe single crystal doped by copper to 10^{18} cm^{-3} yielded a coefficient five times greater than that obtained on a pure CdSe sample.

According to the model of self-diffusion in undoped CdSe samples the diffusion process introduced only ionized vacancies, and the addition of acceptor impurities, such as copper, should decrease the concentration of vacancies and the values of the self-diffusion coefficients of cadmium. Another type of influence of acceptor impurities on the self-diffusion of germanium was found in Refs [9, 10].

REFERENCES

[1] P. M. Borsenberger, D. Stevenson, R. A. Burmeister, *II–VI Semiconducting Compounds*, International Conference, Benjamin, New York 1967.

[2] J. Żmija, M. Demianiuk, *WAT Bull.*, **19**, 77, (217); 9(1970), in Polish.

[3] J. Żmija, *Technology, Structural Defects and Properties of II–VI Semiconducting Compounds*, Appendix to *WAT Bull.*, **2**, 290 (1970), in Polish.

[4] J. Żmija, to be published.

[5] R. F. Erebrick, A. J. Strauss, *J. Phys. Chem. Solids*, **25**, 1441 (1964).

[6] A. N. Niesmeyanov, A. Łapicki, N. Rudenko, *Preparation of Radioisotopes*, PWN, Warsaw 1956, in Polish.

[7] J. Żmija, *Radioisotope Studies of Self-Diffusion in Metals*, Warsaw 1967, in Polish.

[8] W. M. Walenta, C. Ramsatry, *Phys. Rev.*, **106**, 75 (1957).

[9] A. Dreben, *J. Electrochem. Soc.*, **17**, 111, 4 (1964).

[10] P. G. Shewmon, *Diffusion in Solids*, Mc Graw-Hill, New York 1963.

[11] J. Żmija, *WAT Bull.*, **19**, 65, (217); 9 (1970), in Polish.

[12] F. A. Kroger, *The Chemistry of Imperfect Crystals*, North-Holland Publishing Company, Amsterdam 1964.