STUDIES ON THE DIFFUSION OF COPPER, SILVER AND GOLD IN SINGLE-CRYSTALLINE CADMIUM SULFIDE

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The paper brings the results of studies on the diffusion of copper, silver and gold in single-crystalline cadmium sulfide. Investigations were conducted by means of radioactive ^{64}CU, ^{110m}Ag and ^{198}Au tracers. Diffusion proceeded from deposited layers and from the gas phase. The diffusion penetration profiles were determined by the radioactive tracer sectioning technique based on measurements of radiation intensity after the removal of successive layers and the specific activity of the successive layer.

It was found that the diffusion flux of these impurities has two components of interchange (slow) and interstitial (fast) diffusion. This was corroborated by investigations on the resonance frequency of an electroacoustic transducer produced by diffusion of these impurities into appropriately oriented CdS platelets. Interchange diffusion establishes low concentrations of donor states, whereas interstitial diffusion gives high concentrations of acceptors. Examination of the diffusion of silver as a function of partial pressure of sulfur has revealed that when the partial pressure of sulfur decreases the solubility and diffusion coefficients of silver decrease. Diffusion studies for copper and silver from sputtered layers showed that the values of the coefficients of both types of diffusion are lower than the corresponding ones for diffusion from the gas phase at saturated sulfur vapor pressure. Changes of the diffusion coefficients as a function of temperature were studied in the cases of diffusion from the gas phase under sulfur vapor saturation conditions and from deposited layers, and on their basis the activation energies of the relevant diffusion processes were established. It was ascertained that the activation energy of the individual processes increases almost linearly with the square of the diffusing impurity ionic size. A similar dependence had been observed earlier in studies of impurity diffusion in aluminum. The obtained results were elucidated on the basis of the point imperfection theory in the group II–VI semiconducting compounds.

Studies of diffusion of copper in single-crystalline CdS along the [0001] direction and perpendicularly to it exhibited slight anisotropy of this process.

1. Introduction

The noble metals, to which the triad Cu, Ag and Au belongs are important impurities in group II–VI semiconducting compounds. This is due to the fact that they act as active centers in fluorescence phenomena, as coloured centers in their optical properties and as acceptors in transport processes.

The most extensive studies were performed with CdS. In the work described in Ref. [9]

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the effect of doping this substance with Cu, Ag and Au on its fluorescent and optical properties was examined. However, the nature of the defects incorporated by these impurities in the group II–VI semiconducting compounds has not yet been fully recognized. This causes that a reliable assessment of the effect of these defects on their properties, including the electric properties which we are interested in, cannot be made. Although diffusion enables both doping and scrutiny of the nature of the formed defects, no such complete investigations which would lead to general conclusions have been made.

Clarke [1] examined the diffusion of Cu into CdS from sputtered layers by the radioactive tracer sectioning technique. However, he analyzed the obtained diffusion profiles basing on an erroneous assumption that volume diffusion is compensated by some rather enigmatic surface diffusion. The diffusion flux is divided into a volume component (slower) and the so-called surface component (fast), but only the former was analyzed by the Fischer method [2]. The studies were carried out for directions parallel and perpendicular to the [0001] direction, but no anisotropy of the process was revealed.

Woodbury [3] examined the diffusion of silver in CdS single crystals under conditions of saturated vapor pressure of sulfur and cadmium. The diffusion profiles received by him can be divided into three parts. At very low concentrations (10^{11} to 10^{13} Ag atoms per cm^3) a very fast diffusion process is observed and the author suggests that this is interstitial diffusion. At the highest concentrations (2.2×10^{18} Ag atoms per cm^3) the rate of diffusion of silver in single-crystalline CdS is near that of copper in these crystals, observed by Clarke. Diffusion of intermediate rates can be explained by assuming a definite interaction between the interstitial Ag atoms and other point defects. He found that the kind of atmosphere under which the given process occurs bears a considerable effect on the diffusion rate and solubility of the diffusing element. Higher values of diffusion coefficients, but lower solubilites of the diffusing element, are achieved under pressures of cadmium saturated vapors, whereas under conditions of saturated sulfur vapor pressures quite the opposite — lower values of diffusion coefficients and larger values of solubility.

The highest solubility is observed under conditions of firing in an argon atmosphere. Activation energy determinations, however, were made with the use of all obtained diffusion coefficients. This does not seem to be correct, for under different conditions there will be different diffusion mechanisms; hence, the activation energy quoted by Woodbury is a mean value.

The authors believe that the results of diffusion studies for copper and silver in CdS of Clarke and Woodbury are incomparable, for in the former case [1] the process proceeded from sputtered layers of the diffusing element, and in the second case [3] from the gas phase at various compositions of the atmosphere over the fired sample. More general conclusions may be arrived after diffusion studies under identical conditions are made for these impurities in CdS. It seems that from the practical viewpoint studies under sulfur saturated vapor pressure will prove to be the most interesting. There is often the need for conducting diffusion of these elements from sputtered layers and it would, therefore, also be purposeful to perform such studies and compare the obtained results with those with the gas phase studies. This would allow a critical discussion of the results quoted above when general conclusions are drawn.

2. Experimental procedure

The single crystals of cadmium sulfide used in these studies were obtained by the modified Piper Polish technique [4]. The obtained single crystals of 10 to 20 mm diameter and 30 to 60 mm length were oriented by the roentgen method. The samples cut from them had the dimensions $5 \times 5 \times 2.5$ mm, and the larger faces were either (0001) planes or planes perpendicular to the (0001) plane. These single crystals had a density of dislocations of the order of 10^3 to 10^4 per cm^2. The density was determined by means of the
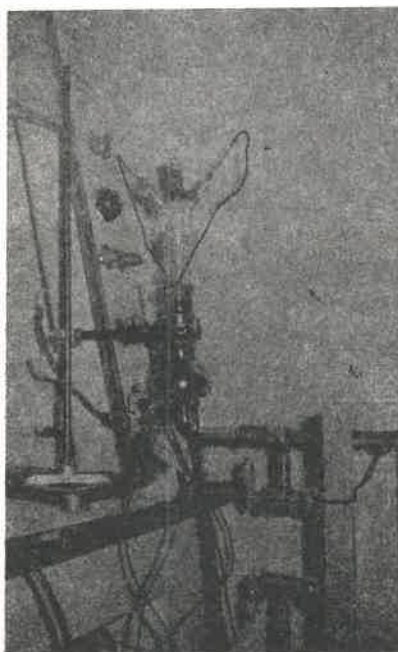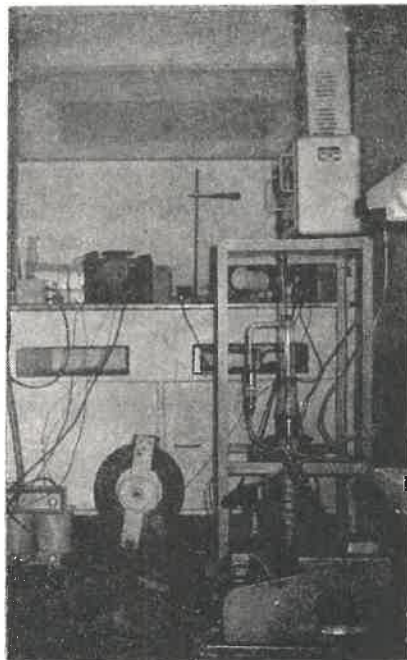

Fig. 1

Fig. 2

Fig. 1. Photograph of dusting device for depositing radioisotopes
Fig. 2. Photograph of arrangement for sealing samples in ampules and firing them

roentgen technique and etch pits [5]. The surfaces of all samples were ground and polish mechanically, and in order to remove any deformations of structure which might be formed during mechanical treatment they were briefly polished chemically in hot orthophosphoric acid.

The diffusion processes proceeded from deposited layers and from the gas phase. Layers of radioisotopes some 0.1 μm thick were deposited in a glass dusting device built for this purpose. The samples, with appropriately weighed portions of components and radioisotopes or with deposited radioisotopic layers, were sealed under vacuum (of the order of 10^{-5} torr) or under a pre-established pressure of neutral gas in quartz ampules. Firing was accomplished in wire-wound heating furnaces in which the resulting thermal equilibrium of the system ensured temperature stabilization within $\pm 10\,°C$. Pt-PtRh thermocouples

connected to the compensator indicator or thermoregulator were used for measuring temperature and its distribution.

After the ampules were removed from the furnace, they and their contents were rapidly cooled in water. In order to eliminate the perturbing effect of surface diffusion phenomena on the measurements a layer of thickness greater than the maximum penetration of diffusion (100 to 500 μm) was removed from all surfaces of the sample except the one reserved for measurements.

Such prepared samples were then sectioned radioisotopically. In the case when the radioactive tracer sectioning was based on measurements of radiation intensity after removal of successive layers, the layers were mechanically ground off on size 400 water-resistant paper. On the other hand, when the activity of the remowed layers were measured, then apart from mechanical working, layers were removed by chemical polishing in 12 n HCl [3].

Measurements of the thickness of the removed layers were made by weighing the samples after removal of the successive layer on a semiautomatic scales of 0.00001 g accuracy. Also, random measurements were made with an Abbe cathetometer.

Gamma radiation intensity measurements were made after a successive layer was removed with a Geiger-Müller counter, type GAH, and a scintillation counter. Specific activity measurements of the polishing solutions were made with a liquid counter, manufactured by Vakutronik, GDR. Pulses from the counters were recorded on a PEL-5 scaler.

Calculations of diffusion coefficient from the run of the diffusion profile determined by specific activity measurements made use of the expression

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

Here, $i(x, t)$ is the specific activity of layers at depth x after time t of firing at constant temperature, and D is the diffusion coefficient. On the other hand, in the case of profiles determined from radiation intensity measurements after removal of a successive layer use was made of the expression

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

where ΔI_n denotes the change in radiation intensity after removal of layer of thickness ΔX_n, while the other notation is the same as for Eq. (1). Both of these expressions are solutions to Fick's second law for the relevant experimental conditions.

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

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \tag{3}$$

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

The diffusion coefficients were calculated from experimental data with the help of Eqs (1) and (2), and the frequency factor D_0 and activation energy E with the help of Eq. (3).

The errors with which these quantities were found were computed by the least squares method using a computer. The probable error when determining the diffusion coefficients does not exceed 20 per cent, while the frequency factor and activation energy are found with an accuracy better than 45 and 5 per cent, respectively.

3. Diffusion of copper

Diffusion of copper was investigated by the radioactive tracer sectioning technique, the radioisotope ^{64}Cu being used. This radioisotope was obtained by irradiation of spectrally pure copper in a reactor. The ^{64}Cu isotope thus obtained decays with a half-life of $T_{1/2} = 12.8$ hrs. It emits 0.571 MeV (13%) and 0.657 MeV (15%) beta rays and 1.34 MeV gamma rays [6].
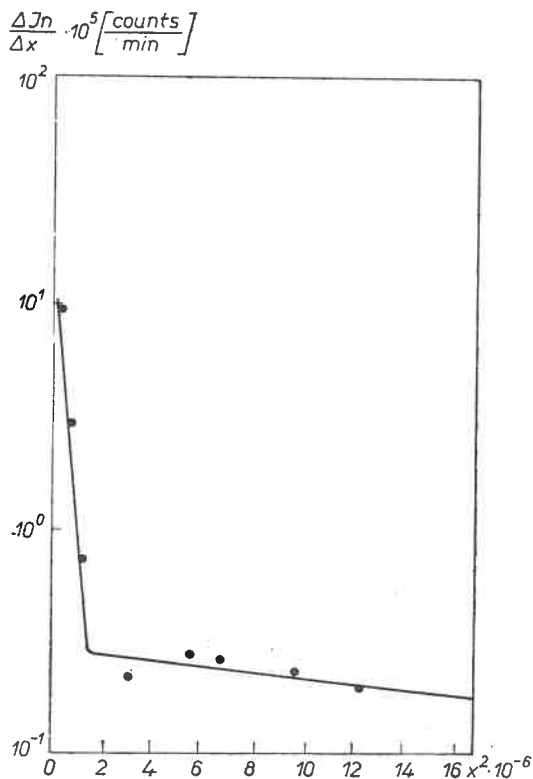

Fig. 3. Typical diffusion profile of copper in CdS single crystals along [0001] direction from the gas phase at 430°C for 65 minutes

Diffusion studies for copper were performed for diffusion from sputtered layers and the gas phase. In the latter case the radioactive sectioning analysis was based on measurements of gamma intensity after each successive layer was removed. A typical penetration profile obtained in this way is shown in Fig. 3, and it distinctly exhibits the two components of diffusion, i.e. the interchange (slow) and interstitial (fast) components. Diffusion proceeding from deposited layers, on the other hand, was examined by measuring

the activity of the removed layers, and the penetration profiles thus found are depicted in Fig. 5. In this case also the diffusion flux has an interchange and an interstitial component. Copper was diffused along directions parallel and perpendicular to the [0001] direction. Diffusion profiles similar to that shown in Fig. 3 were used for determining the
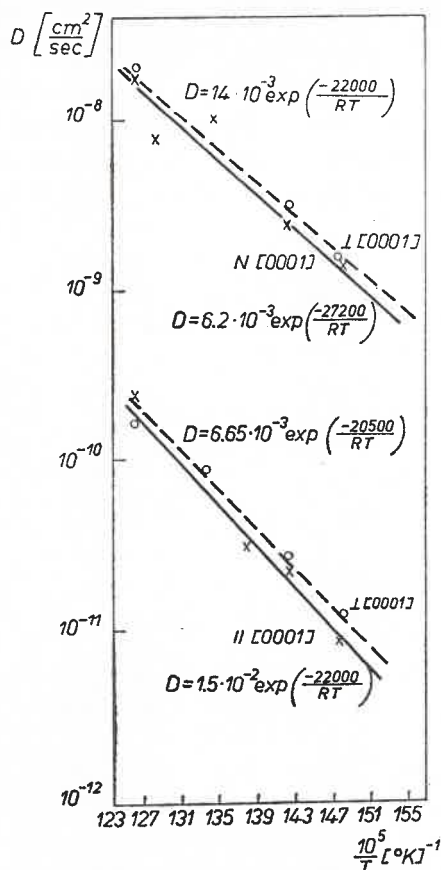

Fig. 4. Temperature dependence of interchange and interstitial diffusion coefficients for copper in CdS single crystals along and perpendicularly to [0001] direction from the gas phase

interchange and interstitial diffusion coefficients for the gas phase case by means of Eq. (2). The temperature dependence of these coefficients for both of the studied crystallographic directions is presented in Fig. 4.

The run of the curves presented in Fig. 4 is described by the following dependences: for interchange diffusion along the [0001] direction

$$D = 6.2 \times 10^{-3} \exp\left(-\frac{27,200}{RT}\right) \tag{4}$$

and in the direction perpendicular to [0001]

$$D = 1.4 \times 10^{-3} \exp\left(-\frac{22,000}{RT}\right) \tag{5}$$

whereas for interstitial diffusion along the [0001] direction

$$D = 1.5 \times 10^{-2} \exp\left(-\frac{22,000}{RT}\right) \qquad (6)$$

and in the direction perpendicular to [0001]

$$D = 6.65 \times 10^{-3} \exp\left(-\frac{20,500}{RT}\right). \qquad (7)$$

On the other hand, profiles such as those in Fig. 5 were utilized in Eq. (1) to determine the coefficient of interchange diffusion from the deposited layers. These coefficients are
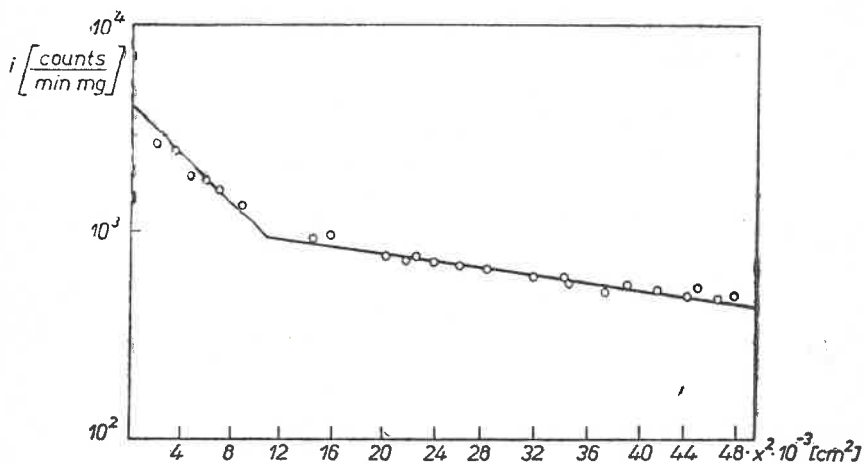

Fig. 5. Typical diffusion profile of copper in CdS single crystals along direction perpendicular to [0001] from sputtered layer of copper under atmospheric pressure of argon at 600° for 6 hrs 45 min

presented as a function of temperature in Fig. 6. As the difference between the coefficients of diffusion along the two crystallographic directions fits within experimental error, the respective type of diffusion is assigned with a single line. The run of these lines is described by the following expression for interchange diffusion

$$D = 0.84 \times 10^{-3} \exp\left(-\frac{16,700}{RT}\right) \qquad (8)$$

and for interstitial diffusion

$$D = 0.2 \times 10^{-3} \exp\left(-\frac{13,000}{RT}\right). \qquad (9)$$

It should be stressed, however, that the coefficients of diffusion of copper in the direction perpendicular to [0001] are somewhat higher than those in the [0001] direction. Also, they have such a distribution that one should expect a lower value of activation energy for diffusion in the former case.

A similar regularity was found to exist for diffusion of copper in CdS from the gas phase. The obtained results show that diffusion from deposited layers features lower values of both diffusion coefficients and their activation energies, alike.

4. Diffusion of silver

Diffusion of silver in CdS single crystals along the [0001] direction was led only from saturated sulfur vapor. Investigation of this process was based on radioactive tracer sectioning with the use of the [110m]Ag isotope. It was obtained by irradiating spectrally pure silver in the flux of slow neutrons of a nuclear reactor. This radioisotope has an intricate decay spectrum [6]. In decaying it emits beta and gamma rays of various energies, the former having a 0.088 to 2.885 MeV range, and the latter a 0.116 to 1.506 MeV range. Diffusion
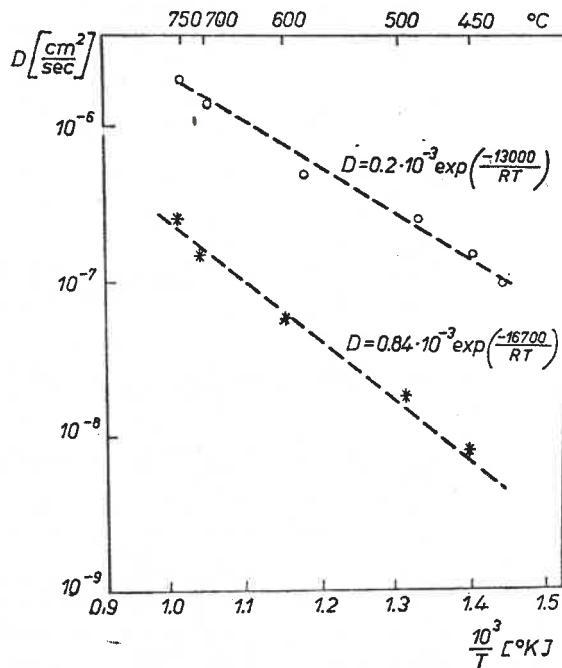

Fig. 6. Temperature dependence of coefficient of diffusion of copper in single-crystalline CdS from sputtered copper layers under atmospheric pressure of argon. O — diffusion along [0001] direction, ✕ — diffusion along direction perpendicular to [0001]

profiles were determined by measuring the specific activities of the removed layers. Thanks to the use of appropriately diluted silver standards [7], the diffusion profiles are expressed in number of Af atoms per cm^3 of examined single crystal. A typical profile is shown in Fig. 7. It was found that the concentration of Ag atoms rendered by both types of diffusion increases when the partial pressure of the sulfur vapor rises. Diffusion under conditions of cadmium saturated vapor pressure gives concentrations three to four orders of magnitude smaller than the concentrations established during firing under conditions of sulfur saturated vapor pressure. Diffusion profiles obtained with samples of different densities of dislocations indicate that both solubility and diffusion coefficients increase together with increasing density. The shapes of the diffusion profiles also show that the concentration of silver atoms in the

interstitial sites becomes established not only as a result of their diffusion from the surface, but also because of equilibrium transitions from the lattice sites, and *vice versa.* The diffusion coefficients were calculated with the use of Eq. (1).

The temperature dependence of the coefficients of interchange and interstitial diffusion obtained from the gas phase at the pressure of sulfur saturated vapor is depicted in Fig. 8.
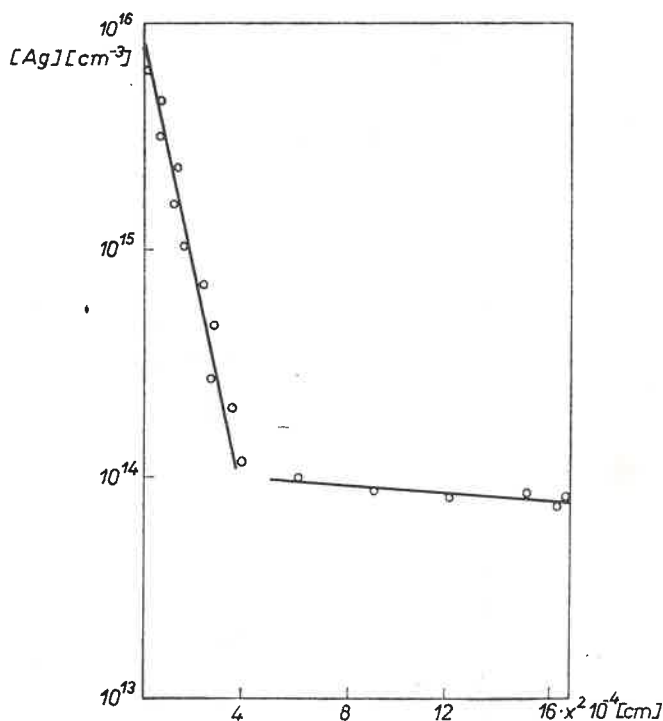

Fig. 7. Typical diffusion profile of silver in single-crystalline samples of CdS conducted under sulfur saturated vapor pressure

The shapes of the curves are described by the following relations:
for interchange diffusion

$$D = 34.8 \exp\left(-\frac{28,900}{RT}\right) \tag{10}$$

and for interstitial diffusion

$$D = 0.2\times10^{-2} \exp\left(-\frac{11,100}{RT}\right). \tag{11}$$

The experimental points do not exhibit such large deviations of the averaged lines as had been observed in study [3]. This straggling is caused by the precipitation of silver on dislocations [8] and the effect of the dislocations on the rate and ease of diffusion.

5. Diffusion of gold

The diffusion of gold in single-crystalline CdS along the [0001] direction was conducted from sputtered layers and from the gas phase under the pressure of saturated sulfur vapor. Investigations were performed by the radioactive tracer sectioning technique, in the first case based on measurements of gamma radiation intensity after removal of successive

The equations visible in the figure:

$$D = 0.2 \cdot 10^{-2} \exp\left(\frac{-11100}{RT}\right)$$

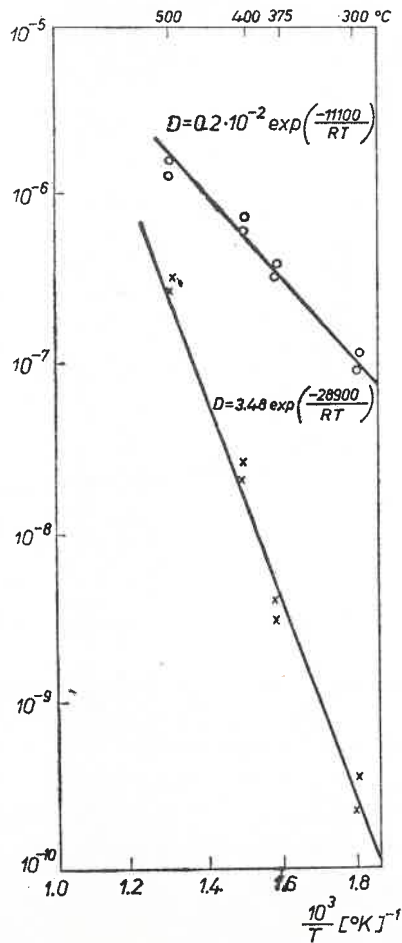$$D = 3.48 \exp\left(\frac{-28900}{RT}\right)$$

Fig. 8. Temperature dependence of coefficients of interchange and interstitial diffusion of silver in CdS single crystals along [0001] direction under sulfur saturated vapor pressure

layers, and in the second on measurements of the specific activities of the removed layers. The [198]Au isotope was used as the tracer. It was obtained by irradiating spectrally pure gold in the neutron flux of the EWA nuclear reactor. This radioisotope, decying with a half-life of $T_{1/2} = 2.69$ days, emits beta particles of energies from 0.29 to 1.38 MeV and gamma rays of energies from 0.41 to 1.08 MeV [6]. The diffusion profiles obtained in this case were similar to those observed in examinations of the diffusion of copper and silver in CdS single

crystals. The coefficients of interchange and interstitial diffusion were determined by means of Eqs (1) and (2). The dependence of these coefficients on temperature for the diffusion from sputtered layers is shown in Fig. 9, whereas for the diffusion from the gas phase at
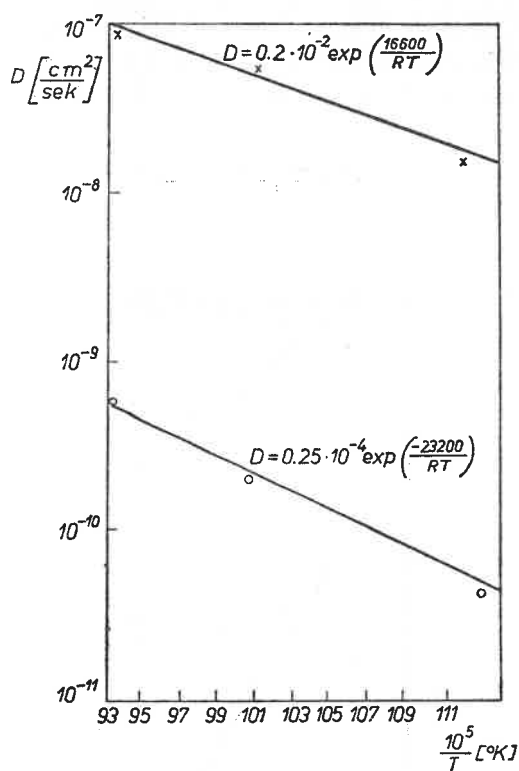

Fig. 9. Temperature dependence of coefficients of interchange and interstitial diffusion from sputtered gold layers in CdS single crystals along [0001] direction

sulfur saturated vapor pressure in Fig. 10. The run of these lines presented in the former figure can be described by the following dependences:

for interchange diffusion

$$D = 0.25 \times 10^{-4} \exp\left(-\frac{23,200}{RT}\right) \tag{12}$$

and for interstitial diffusion

$$D = 0.2 \times 10^{-2} \exp\left(-\frac{16,600}{RT}\right). \tag{13}$$

On the other hand, the lines presented in Fig. 10 are described by the dependences:
for interchange diffusion

$$D = 0.07 \exp\left(-\frac{31,600}{RT}\right) \tag{14}$$

and for interstitial diffusion

$$D = 0.15 \times 10^{-2} \exp\left(-\frac{15{,}300}{RT}\right). \tag{15}$$

As in the case of copper, the activation energy of diffusion of gold from sputtered layers is lower than that for diffusion from the gas phase under the pressure of saturated sulfur vapor. The diffusion coefficients, however, are comparable in both cases. Notwithstanding,
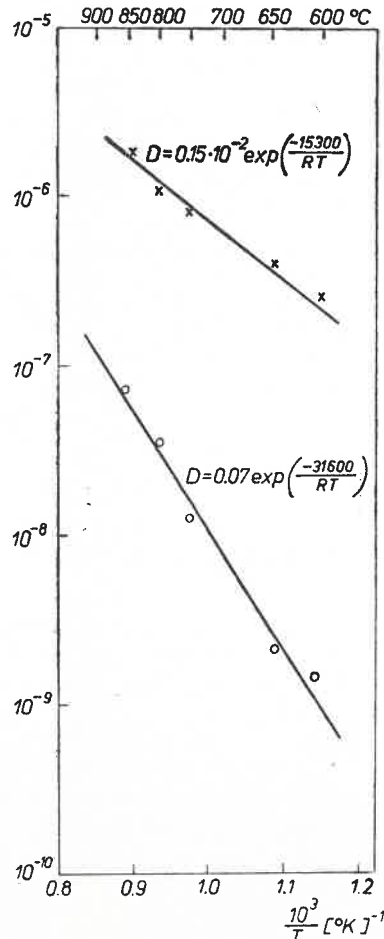

Fig. 10. Temperature dependence of coefficients of interchange and interstitial diffusion of gold in CdS single crystals along [0001] direction under sulfur saturated vapor pressure

it should be remembered that diffusion studies for gold from sputtered layers are rather tentatively treated here. The samples used had undetermined dislocation density and purity, the shape of the curve was established on the basis of a small number of experimental points.

The interchange diffusion of copper, silver and gold in CdS single crystals was also examined by the acoustic method. The depths of diffusion along the [0001] direction at a temperature of 400°C obtained by this method are in agreement with those found by the radiotracer technique. Thus, this is a corroboration of the correctness of the way in which the results of the radiotracer analysis were prepared. Comparable values of interchange diffusion coefficients were also acquired. Similar conclusions are also arrived at from the results of preliminary investigations with an electron mirror microscope [5].

6. Discussion of results and conclusions

The performed investigations on the diffusion of copper, silver and gold in single crystals of cadmium sulfide have shown that the diffusion of these impurities possesses two components, interchange (fast diffusion) and interstitial (slow diffusion). At certain temperatures the differences between the coefficients of interstitial and interchange diffusion are contained within one or two orders of magnitude. Interchange diffusion establishes low concentrations of donor states whereas interstitial diffusion high concentrations of acceptors. In studies of the diffusion of silver in single-crystalline CdS it was found that this difference depends on the density of dislocations. The conception of two diffusion components was confirmed by diffusion studies by the acoustic method and preliminarily by means of an electron mirror microscope. The values of both diffusion coefficients depend on the conditions under which these processes occur.

The studies on diffusion of silver from the gas as a function of sulfur partial pressure showed that with decreasing partial pressure of sulfur the solubility and diffusion coefficients decrease. Moreover, the diffusion of copper and gold from sputtered layers of these elements was also investigated. It was ascertained that in principle the values of the coefficients for these two types of diffusion are lower than the corresponding values for diffusion proceeding from the gas phase under the pressure of saturated sulfur vapor. When investigating self-diffusion of cadmium from the gas phase in single crystals of group II–VI compounds [5] a similar behaviour of the self-diffusion coefficients as a function of partial pressure of the oxygen group elements was observed. This stems from the fact that together with a decrease in the pressure of the sulfur vapor there is a drop in the concentration of cadmium vacancies, what slows down diffusion. Under the conditions of saturated sulfur vapor pressure the concentration of the sulfur vacancies V_S is higher than that of the cadmium vacancies V_{Cd}, whereas under the pressure of cadmium or impurity metal this relationship is exactly the opposite.

When these reguarities become established a certain role is also played by the complexes which these impurities may form with other point defects in the group II–VI semiconducting compounds. One such possible complex is an impurity at an interstitial site and a cadmium vacancy. This kind of complex may fall apart by the transition of the impurity atom to the cadmium vacancy (an impurity in the substitutional position) [10]. Vacancies may form both on the surface of a sample or inside it. The sources and sinks of vacancies are surface and interior boundaries. Their action may provide an explanation of the changes in physico--electrical properties which are unexplainable when basing on measured coefficients and

constants of diffusion. The time during which equilibrium is achieved is much shorter than that calculated on the basis of diffusion measurements. Should complexes containing more than one impurity atom be taken into account, then it has an effect on the run of the diffusion profile and the temperature dependence of the diffusion coefficients for the impurities.

Diffusion studies performed for copper in single-crystalline CdS from the gas phase and the sputtered layers alike in the direction concordant with and perpendicular to the [0001] direction have revealed a perceptible anisotropy of this effect. The diffusion coefficients are higher and the activation energy lower for the latter case. This anisotropy does not tally
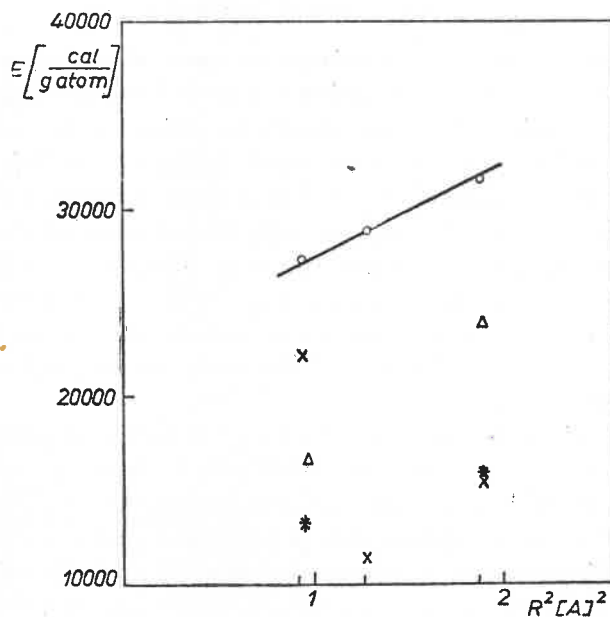

Fig. 11. Dependence of activation energy of diffusion of noble metals in CdS single crystals along [0001] direction upon square of ionic radius. ◯ – interchange diffusion from the gas phase under sulfur saturated vapor pressure, × – interstitial diffusion from the gas phase under sulfur saturated vapor pressure, △ – interchange diffusion from sputtered layers, ✳ – interstitial diffusion from sputtered layers

with the anisotropy of self-diffusion of cadmium in CdS single crystals [5]. Thus far, this diffusion anisotropy is above comprehension. It may be caused either by various forces acting during impurity diffusion and self-diffusion, or by a certain effect of dislocations on these processes. A distinct influence of the density of dislocations on the character of the self-diffusion anisotropy in zinc single crystals was ascertained in study [11].

The studies on the diffusion of the impurities Cu, Ag and Au in cadmium sulfide single crystals revealed the effect of the size factor of the diffusing element on these processes. The effect of this factor on the diffusion of impurities in aluminum and its diluted alloys was observed in the work [12]. It was found that the activation energy of diffusion increases linearly with an increase of the square of the ionic radius of the diffusing element. To get a more general analysis of the influence of the size factor on the diffusion of impurities in

cadmium sulfide single crystals, plots were made of the activation energy as a function of the square of the ionic radii of the diffusing elements. Figure 11 presents such a dependence for the diffusion of impurities in CdS single crystals. The sizes of the ions with a single positive charge were taken from Ref. [13].

It is evident from this graph that the activation energies of interchange and interstitial diffusion under conditions of sulfur saturated vapor pressure increase nearly linearly with an increasing squared ionic radius of the diffusing element. This approximation is rather rough owing to the small number of experimental points. The activation energies of the impurities from sputtered layers exhibit similar tendencies in the dependence on ionic size of the diffusing impurities. It must be said that the linearity of the dependence between activation energy and the square of the diffusing impurity ion radius in pure aluminum is also valid for diffusion of impurities in single crystals of cadmium sulfide. The small ionic size of copper explains the extreme ease and hig rate of interchange and interstitial diffusion in these single crystals.

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