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STUDIES ON THE DIFFUSION OF GOLD, SILVER AND COPPER IN CdS AND CdSe SINGLE CRYSTALS BY A METHOD BASED ON MEASUREMENTS OF THE RESONANT CAPACITANCE OF PIEZO-ELECTRIC TRANSDUCERS

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The paper presents the results of studies on the diffusion of copper, silver and gold in single-crystalline CdS and CdSe made by methods based on determinations of the frequency-response characteristics of transducers produced *via* diffusion. The capacitance of the transducers was measured at frequencies somewhat below and above the resonant frequency, and taken together with the measured frequency-response of the capacitance changes this allowed the resistance distribution along its axis to be determined. The diffusion coefficients calculated from these data agree with those obtained by the radiotracer technique for the slow component (interchange diffusion).

1. *Introduction*

The basic operation in the production of many electronic devices (*e. g.*, solar batteries) and electron-phonon devices (*e. g.*, diffusion layer piezoelectric transducers produced from single crystals of semiconducting II–VI compounds of wurtzite type structure) is the incorporation by diffusion of one of the noble metals (copper, silver or gold) into the initial material. As a result of this process a thin layer featuring a low concentration of current carriers is formed in the appropriately oriented single-crystalline plate. The thickness of the layer limits the region in which the concentration of deep compensating acceptor levels predominates. The atoms of noble metals in the structure of single-crystalline II–VI compounds may be incorporated in the place of the atoms of the group II element, or interstitially. In the first case they should give acceptor levels mainly due to the deficiency of valence electrons of these impurities relative to the group II component. The latter type of incorporation gives donor levels. Of the triad of noble metals, copper has the smallest ionic radius, and therefore should enter easily interstitial sites.

Radioisotopic studies show [1] that the component of interstitial diffusion, as compared with interchange diffusion, usually features higher diffusion coefficients at appropriate temperatures and lower values of activation energy. The diffusion profiles are characterized

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by the larger share of interchange diffusion at the sample's surface layer and the drop of this share with a simultaneous rise of the interstitial component with increasing depths of the layer under consideration.

A piezoelectric transducer operating on the principle of diffusion layers in single-crystalline CdS and CdSe is [2] a low resistance platelet of this material in which a high-resistance diffusion layer was formed on one of the surfaces being a (0001) plane. If an alternating electric field is applied to this surface, the drop in the applied voltage takes place primarily on the diffusion layer. Since CdS and CdSe single crystals are piezoelectric, the voltage drop causes deformations in them which are accompanied by mechanical stresses. The performance of such a diffusion layer of increased resistivity is like that of an ordinary X-cut quartz transducer. The thickness d of the piezoelectric transducer's active layer is linked with its resonant frequency ω_n by the following dependence:

$$d = n\frac{V_l}{2\omega_n} \tag{1}$$

where $n = 1, 2, 3, \ldots$ is the number of the successive harmonic, and V_l is the velocity of propagation of longitudinal ultrasonic waves in the given material.

For diffusion of impurities from a solid source into a semi-bound space the high-resistance layer thickness d, the diffusion coefficient D and the diffusion time t are related to each other by the dependence [3]

$$d = \sqrt{Dt} \tag{2}$$

assuming that over the distance d the concentration of the diffusing substance decreases two-fold in comparison with its value at the surface. Apart from this, the thickness d of the considered layer can be found from the well known formula

$$d = \frac{\varepsilon}{4\pi C} \tag{3}$$

where ε is the permittivity of the semiconducting material, and C is the measured specific capacitance of the layer.

Moreover, it is usually assumed that the resistivity of the diffusion layer is infinitely high, while the layer itself has a distinct boundary with the low-resistance region of the platelet [4, 5]. In reality, we always deal with a distribution of resistivity conditioned by the diffusion phenomena. In this case there are limits of resistivity values ϱ_k which correspond to the coordinate X_k dividing the layer into high- and low-resistance parts. To each value of C_0, at a given function $\varrho = \varrho(x)$, there corresponds a definite value $C = C(\omega)$ and a certain effective thickness of the diffusion layer, $d_{\text{eff}} = d_{\text{eff}}(\omega)$, which is described by the formula [6]

$$d_{\text{eff}}(\omega) = \frac{\varepsilon}{4\pi C(\omega)}. \tag{4}$$

When determining the relation $\varrho = \varrho(x)$ use is made of the formulae

$$x = \frac{\varepsilon}{4\pi C(\omega)} \quad \text{and} \quad \varrho(x) = \frac{4\pi}{\varepsilon\omega}. \tag{5}$$

Figure 1 depicts the general form of the function $\varrho = \varrho(x)$, where on the ordinate axis the values of reciprocal frequency and resistivity are laid off, whereas the abscissa axis carries the X coordinate. The frequency f and the value of ϱ which is the boundary between the low- and high-resistance regions of the platelet are associated by the relation [6]

$$\frac{1}{f} = \varrho \frac{\varepsilon}{2}. \tag{6}$$

The curve going through the origin of the coordinate system and the point with the coordinates $\left(d_0, \frac{1}{f}\right)$ reflects the half-wavelength thickness of the platelet, d_0, of a resonant frequency f_0 according to the relation

$$\frac{1}{f_0} = \frac{2 d_0}{V_l}. \tag{7}$$

We can see from the figure that three effective thicknesses of the diffusion layer, d_1, d_2 and d_0, correspond to three different values of frequency, f_1, f_2 and $f_0 (f_2 > f_0 > f_1)$. It follows thus that determination of the effective thickness from the measured capacitance of the

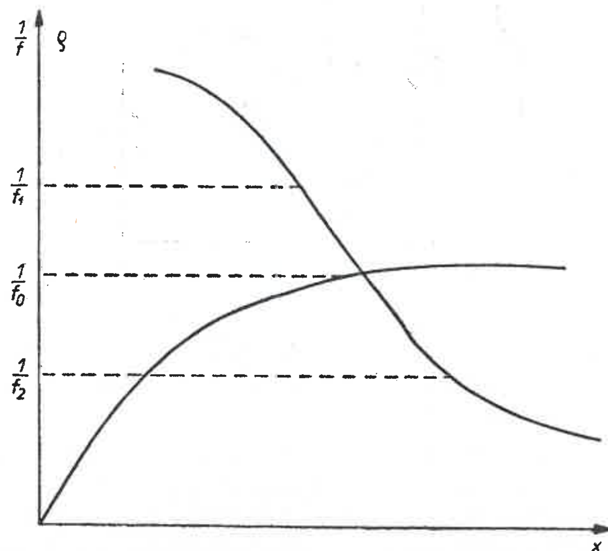

Fig. 1. General form of resistivity distribution over the thickness of the transducer platelet

diffusion layer at a frequency lower than the resonant frequency f_1 gives an overestimated natural frequency of the transducer $(d_1 < d_0)$, whereas at a frequency higher than the resonant frequency it is undervalued. Hence, the resonant thickness of the diffusion layer may be determined either by making several (*e. g.*, two) measurements of its capacitance at frequencies near resonance, or graphically, the latter requiring knowledge of the distribution $\varrho = \varrho(x)$ in the platelet. Knowledge is required of the constants ε and V_l for the material in which such investigations are being performed. In the present work the first method

was used for determining the resonant diffusion layer thickness and then for calculating the diffusion coefficients; the other method was used only in studies on the diffusion of copper in CdS single crystals.

2. *Experimental*

The experiments were made with low-resistance ($\varrho \approx 1$ ohm-cm) single-crystalline CdS and CdSe platelets of the dimensions $10 \times 10 \times 2$ mm. The two largest parallel surfaces of the samples were (0001) planes. To one of these surfaces of each sample, after polishing, a film of copper, silver or gold of a thickness of about 0.1 μ m was sputtered under vacuum (10^{-4} torr). The deposited layer was a circle 1.2 or 7 mm in diameter. The diffusion firing was accomplished in a vacuum furnace in three ten minute periods at 400°C. In order to have ohmic contact the other side of the platelet had indium deposited on it. After each firing the diffusion capacitance was measured at a frequency somewhat below and above the resonant frequency and the resonant diffusion layer thickness was calculated. This type

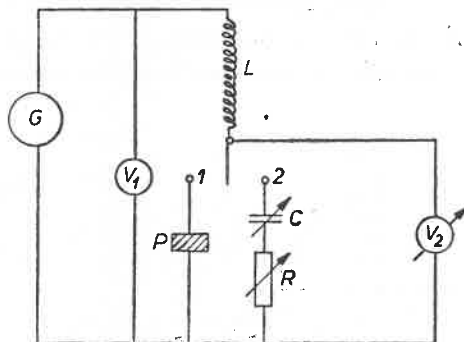

Fig. 2. Arrangement for diffusion studies by the acoustic method

of measurement was performed with the 1.2 mm dia. layer of sputtered diffusing element. Measurements were made by means of the arrangement presented in Fig. 2. In this circuit, sinusoidal voltage from the generator G is fed to the series circuit consisting of the inductance L, the capacitance of the diffusion layer C and the loss conductance of this layer R (switch P in position *1*). By retuning the generator the resonant frequency of the circuit was established according to the readings of the voltmeters V_1 and V_2. Next, by means of the adjustable capacitances C' and resistances R' (switch P in position *2*) the circuit is brought to the resonant state in such a way that the readings of the voltmeters V_1 and V_2 are the same as those set in the previous operation. It is then possible to state that $C' = C$ and $R' = R$. In turn, using Eq. (3) the values of the resonant diffusion layer thickness are determined, and the diffusion coefficients calculated from Eq. (2).

The results of the diffusion studies for copper, silver and gold in CdS single crystals obtained in this way are arranged in Table I, and those for the CdSe single crystals in Table II.

The method requiring knowledge about the distribution $\varrho = \varrho(x)$ was used for studies on the diffusion of copper in CdS single crystals. After each firing the capacitance of the diffusion layer was measured as a function of frequency, $C = C(\omega)$, in the 1 kHz to 200 MHz

TABLE I

Results of studies on the diffusion of copper, silver and gold in CdS single crystals at 400°C

Impurity / Calculated quantities		Copper	Silver	Gold
C_0F	I	$8.8 \cdot 10^{-12}$	$4.65 \cdot 10^{-11}$	
	II	$4.28 \cdot 10^{-12}$	$2.3 \cdot 10^{-11}$	
	III	$1.95 \cdot 10^{-12}$	$1.45 \cdot 10^{-11}$	$5.8 \cdot 10^{-11}$
d_0 (cm)	I	$0.8 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	
	II	$1.6 \cdot 10^{-3}$	$3.1 \cdot 10^{-4}$	
	III	$3.6 \cdot 10^{-3}$	$4.8 \cdot 10^{-4}$	$12 \cdot 10^{-4}$
D cm^2/sec	I	$1.11 \cdot 10^{-9}$	$4.3 \cdot 10^{-11}$	
	II	$2.1 \cdot 10^{-9}$	$8.4 \cdot 10^{-11}$	
	III	$7.3 \cdot 10^{-9}$	$12.3 \cdot 10^{-11}$	$8.1 \cdot 10^{-12}$
Mean diffusion coefficients ultrasonic technique		$3.5 \cdot 10^{-9}$	$4.9 \cdot 10^{-11}$	$8.1 \cdot 10^{-12}$
Diffusion coefficient, radiotracer technique (from gas phase)		$3 \cdot 10^{-9}$ from deposited layer		$2 \cdot 10^{-12}$

I – value determined after 10 minute period of diffusion,
II – value determined after 20 minute period of diffusion,
III – value determined after 30 minute period of diffusion.

TABLE II

Results of studies on the diffusion of copper, silver and gold in CdSe single crystals at 400 °C

Impurity / Calculated quantities		Copper	Silver	Gold
$C_0 (F)$	I	$9.5 \cdot 10^{-12}$	$3.4 \cdot 10^{-11}$	
	II	$3.4 \cdot 10^{-12}$	$1.75 \cdot 10^{-11}$	
	III	$2.1 \cdot 10^{-12}$	$7.2 \cdot 10^{-11}$	$2.31 \cdot 10^{-11}$
d_0(cm)	I	$7.4 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	
	II	$2.1 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	
	III	$33.2 \cdot 10^{-4}$	$9.8 \cdot 10^{-4}$	$3 \cdot 10^{-4}$
	II	$9.1 \cdot 10^{-10}$	$7.8 \cdot 10^{-11}$	
D cm^2/sec	III	$6.3 \cdot 10^{-9}$	$5.4 \cdot 10^{-10}$	$4.8 \cdot 10^{-11}$
Mean diffusion coefficients ultrasonic technique		$3.6 \cdot 10^{-9}$	$3.5 \cdot 10^{-10}$	$4.8 \cdot 10^{-11}$
Diffusion coefficient, radiotracer technique (from gas phase)		$1.2 \cdot 10^{-10}$	$5 \cdot 10^{-10}$	

I – value determined after 10 minute period of diffusion,
II – value determined after 20 minute period of diffusion,
III – value determined after 30 minute period of diffusion.

range. Measurements in the 1 kHz to 1 MHz range were made on samples with a 10 mm dia. circle of sputtered copper, whereas in the 1 to 200 MHz range on samples with copper layers of 1.2 mm diameter. Measurements were performed on three samples of each type. Figure 3 shows the distribution of resistivity in the transducer platelet calculated on the basis of formula (5), use being made of the experimental $C = C(\omega)$ relation. The experimental results are marked appropriately in the figure: X are for a 10-minute firing (curve *1*), O are for a 20-minute firing (curve *2*) and Δ are for a 30-minute firing (curve *3*). The dashed curve defines the frequency-dependence of the diffu-

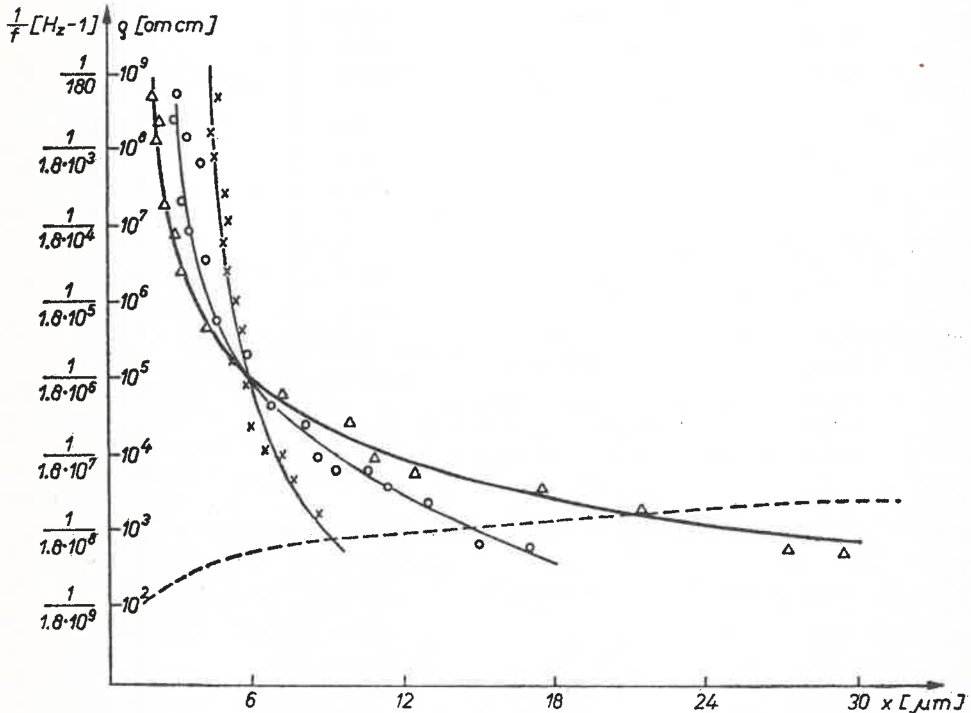

Fig. 3. Distribution of resistivity in transducer platelet calculated on the basis of Eq. (5), using experimental $C = C(\omega)$ after diffusion of copper for: $\times$ — 10 min, $\bigcirc$ — 20 min and Δ — 30 min

sion layer thickness at resonance. It follows from this figure that after the first firing the layer becomes resonant at a frequency of 200 MHz, after the second firing at 150 MHz, and after the third firing at 100 MHz. The corresponding resonant thicknesses are: 11 μm after the first firing, 15 μm after the second firing, and 22 μm after the third firing. The values of the respective diffusion coefficients, calculated from Eq. (2), are: 0.67×10^{-9} cm²/sec, 1.8×10^{-9} cm²/sec and 8×10^{-9} cm²/sec.

3. Analysis of results and conclusions

In the studies on the diffusion of copper in CdS single crystals by determining the resonant thickness of the transducer obtained by this diffusion from measurements of its capacitance at frequencies a little above and below the resonant frequency, and by the

method of determining the resistivity distribution, the results obtained are similar. On this basis, subsequent studies on diffusion (silver and gold in CdS single crystals and copper, silver and gold in CdSe single crystals) were carried out with the former method only. It was established that the mean values of diffusion coefficients conform with the coefficients

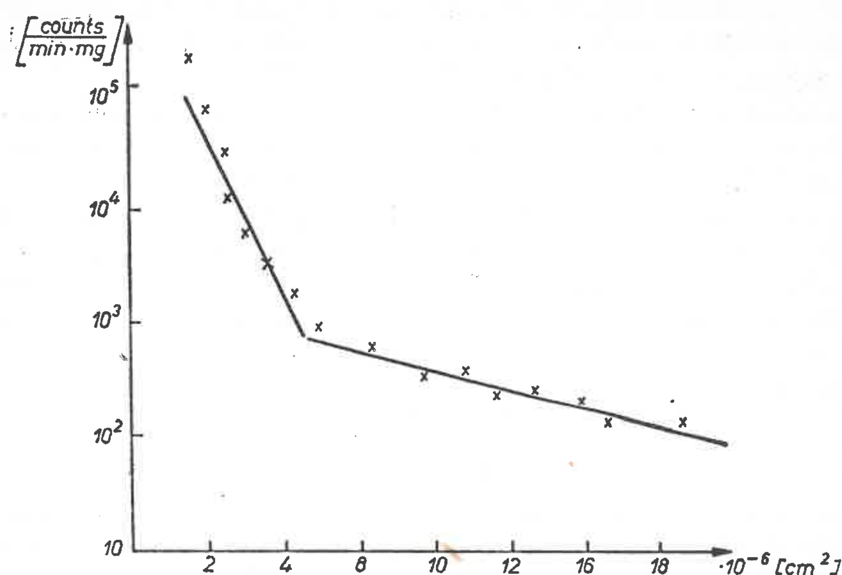

Fig. 4. Profile of diffusion of copper in single-crystalline Cds sample, obtained by the radioactive tracer technique after 30 min period of diffusion from sputtered copper layer 0.2 μm thick at 400°C

determined by the radioactive tracer techniques when diffusion proceeds from a deposited layer of the diffusing element. A rather good agreement was found to exist between the value of resonant thicknesses for the obtained transducers and the mean penetration depth of the predominant interchange diffusion found on the basis of the radioactive tracer sectioning technique. As a illustration, Fig. 4 presents the profile of changes in the concentration of radioactive copper along the CdS sample after 30 minutes of diffusion from a copper layer 0.2 μm thick sputtered on it. This profile is satisfactorily in conformity with the calculated of changes in transducer resistivity and the resonant thickness determined by the methods described here. This corroborates the hypothesis that in semiconducting II–VI compounds the diffusion flux has two components, namely, interchange and interstitial diffusion. In the first case, when the diffusing element substituting the group II component has a deficiency of electrons — as observed in the diffusion of noble metals in CdS and CdSe single crystals — the incorporated impurity gives compensating acceptor levels. On the other hand, when these impurities become incorporated interstitial, they give donor levels. In the case when the interchange component predominates in the resultant flux of a given layer, there is a rise in resistivity. On the other hand, when the interstitial component predominates, the resistivity is decreased as compared with its initial value.

The mean values of interchange diffusion coefficients determined by the radiotracer techniques under conditions of diffusion from the gas phase are not in conformity with those

obtained by the methods described here. For instance, radiotracer studies on the diffusion of silver from the gas phase under saturated sulfur vapor pressure gave a higher value of diffusion coefficient than the mean value of diffusion coefficient obtained in the foregoing. This is because an increase in the pressure of the group VI element's vapor brings about a rise in the number of vacancies after the group II component, what in turn causes an increase in the diffusion coefficient of the impurities replacing the group II component in the semiconducting II–VI compounds.

It was observed that in the case of every impurity the interchange diffusion cofficients become larger with longer firing times. This may be due to a departure from the assumed model, expressed in an unexact form of the assumed formula, or it may be caused by an exchange of the interstitialcy type. The probability of the latter mechanism increases with an increase in the concentration of impurity atoms in the interstitial lattice positions.

The differences in the diffusion coefficients for the different impurities are due to their various ionic radii. The diffusion coefficient is smaller when the ionic radius is larger. This dependence was also observed in radioisotopic studies made for these impurities in CdS and CdSe single crystals.

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