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Correlation of Cu and V_{Zn} concentration within the diffusion region of ZnSe monocrystals

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ABSTRACT

In the paper both the diffusion of Cu ions in ZnSe monocrystals of $M_{1-y}X$ type as well as its influence on the concentration of cation vacancy have been investigated. For the purpose of the investigation the phenomenon of luminescence was used since the diffused impurity by acting on the native defects of the crystal was found to have caused the formation of complexes e.g. centres of luminescence. Thus we can have a few diffusion mechanisms.

Keywords: diffusion, luminescence, point defects.

1. INTRODUCTION

The introduction of a foreign atom F into the lattice of a compound MX has an extremely marked effect on its various physical properties, mainly electrical and optical ones. These changes caused by the formation of complexes between the atoms of the impurity and the native defects of the monocrystals. In such a situation it is essential to take into account a possible presence of several diffusion mechanisms. Namely, the diffusion of Cu in ZnSe monocrystals takes place by means of two mechanisms - the vacancy mechanism and interstitial mechanism of the collinear type¹. Between the diffused Cu concentration and the concentration of cation vacancy in ZnSe there exists a close relationship.

2. EXPERIMENTAL

All the ZnSe monocrystals studied in the present investigations were obtained from Military University of Technology in Warsaw. The samples of the monocrystals studied for the diffusion of Cu were pretreated in the vapour of the anion component. This pretreatment, on one hand, assured a considerable lowering of the number of interstitial atoms and Zn ions and, on the other hand, it increased the concentration of vacancies in the cation sublattice. The ZnSe monocrystals pretreated in such a way showed an actual deficiency of the metal thus forming a compound of $M_{1-y}X$ type.

Cu diffusion was carried out in sealed quartz ampules at the pressure of saturated selenium vapour. The doping source was a film of Cu vacuum-sprayed onto the surface of the samples investigated.

On the basis of the two-sample luminescence method measurements were made of the diffusion coefficients of Cu in ZnSe at temperatures: 773 K, 878 K and 973 K. The method is based on the fact that for a given crystal there is a precisely defined and always the same limiting concentration at which the luminescence appears. For two samples taken from the same crystal and subjected to diffusion under the same physical conditions but with different diffusion annealing times the luminescence front of the sample penetrates to a depth of x_1 in time t_1 and that of the other sample to a depth of x_2 in time t_2 . Then we obtain the following equation²:

$$D = \frac{|x_1^2 t_2 - x_2^2 t_1|}{2 t_1 t_2 \ln(t_2 / t_1)} \quad (1)$$

All the quantities on the right-hand side of (1) can be determined experimentally. Thus the above equation can be used for measurement of impurity diffusion coefficients in semiconductors in which the impurity produces luminescence centres.

3. RESULTS

The diffusion of Cu was carried out on samples of ZnSe which as a result of pretreatment were characterized by an actual deficiency of metal (Zn_{1-y}Se). The introduction of a cation impurity of a valency lower than that of the parent cations has such an effect that with an increase in the impurity concentration, a fall in the ion defect concentration and an increase in the electron defect concentration occur. The cation vacancy concentration, assuming that $[\text{Cu}'_{\text{Zn}}] \gg [\text{V}''_{\text{Zn}}]$, may be expressed by the equation¹

$$[\text{V}''_{\text{Zn}}] = \frac{\text{const}}{[\text{Cu}'_{\text{Zn}}]^2} p_{\text{Se}_2}^{1/2} \quad (2)$$

from which it is seen that the concentration of cation vacancies in a solid solution $\text{Cu}_2\text{Se-Zn}_{1-y}\text{Se}$ decreases with an increase of the concentration of ions Cu^+ .

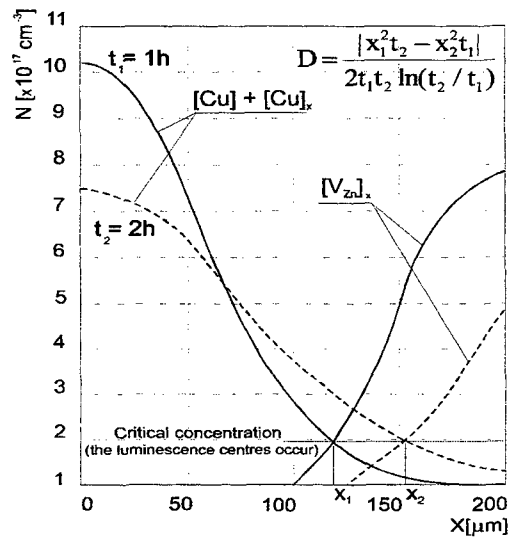


Fig.1. Cu and V_{Zn} concentration profiles for two ZnSe samples at 773 K, $D_{\text{Cu}} = (4.45 \pm 2.48) \cdot 10^{-9} \text{ cm}^2/\text{s}$

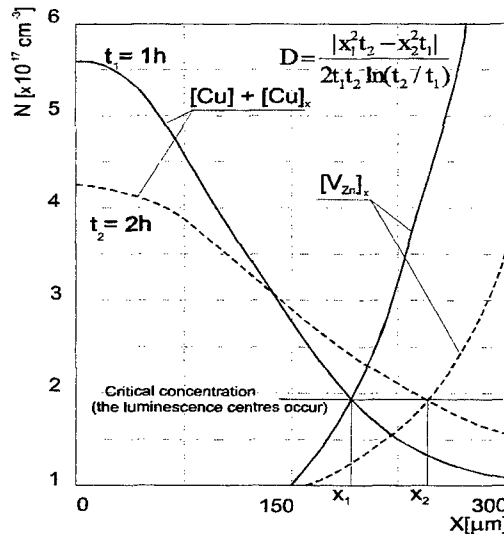


Fig.2. Cu and V_{Zn} concentration profiles for two ZnSe samples at 873 K, $D_{\text{Cu}} = (1.63 \pm 0.39) \cdot 10^{-8} \text{ cm}^2/\text{s}$

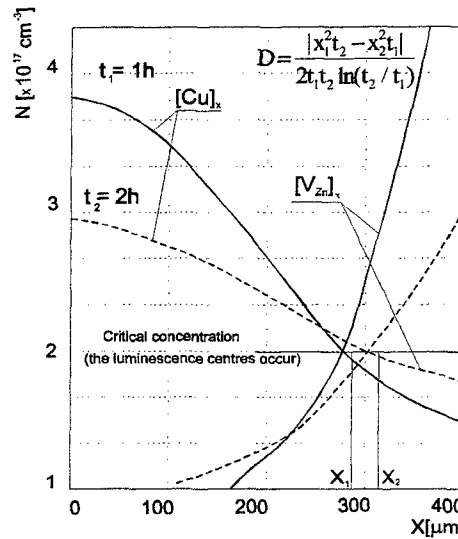


Fig.3. Cu and V_{Zn} concentration profiles for two ZnSe samples at 973 K, $D_{Cu} = (5.40 \pm 0.54) \cdot 10^{-8} \text{ cm}^2/\text{s}$

The relationship between concentration of cation vacancies and the concentration of Cu ions in diffused ZnSe sample may be considered in the following way. Let's assume the denotations below:

- [Cu] - Cu concentration in the initial material,
- $[Cu]_x$ - Cu concentration at depth x in the sample after the diffusion process,
- $[Cu]_0$ - Cu concentration on the surface of sample after the diffusion process.

The concentration distribution of Cu in ZnSe sample is expressed by the following equation:

$$\frac{[Cu]_x - [Cu]}{[Cu]_0 - [Cu]} = \frac{h}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (3)$$

Based on equation (2) the relationship between the concentration of cation vacancies in the initial sample $[V_{Zn}]$ and that on the depth x from its surface after the diffusion process $[V_{Zn}]_x$ may be expressed as follows:

$$[V_{Zn}]_x = [V_{Zn}] \frac{[Cu]^2}{[Cu]_x^2} \quad (4)$$

On the basis of the measured values of Cu diffusion coefficients and knowing that: $h=1\mu\text{m}$, $[Cu]=1.0 \cdot 10^{17} \text{ cm}^{-3}$, $[Cu]_0=6.5 \cdot 10^{19} \text{ cm}^{-3}$ and $[V_{Zn}]=8.2 \cdot 10^{17} \text{ cm}^{-3}$, it was possible to create profiles of the distribution concentration for both the impurity $[Cu]_x$ and $[V_{Zn}]_x$ of the compound. The graphs of equations (3) and (4) were depicted in fig.1., fig.2. and fig.3. for ZnSe samples doping Cu at 773 K, 873 K and 973 K respectively. It can be seen that $[Cu]_x=f(x)$ and $[V_{Zn}]_x=f(x)$ curves intersect at such an impurity concentration that will form luminescence centres independent of the temperature process. Furthermore, the course of the curves suggests that the intersection point i.e. the point where the concentration of Cu activator equals the concentration of cation vacancies and where the luminescence front occurs, we have a transition from the region of higher conductivity to the compensated region of lower conductivity. This fact was proved strictly by Aven and Halsted³.

4. CONCLUSIONS

The result of the investigations and the analysis of the correlation of the concentrations of both Cu impurity and cation vacancies in the ZnSe diffusion region made it possible to conclude that Cu diffusion in the compound followed two distinct mechanisms: a vacancy mechanism at Cu concentration a little above $2 \cdot 10^{17} \text{ cm}^{-3}$ and an interstitial mechanism of collinear type at higher concentrations.

In the case under discussion in the present paper, Cu is diffused into a compound of the $M_{1-y}X$ type, i.e. a compound containing a high concentration of cation vacancies $[V''_{Zn}]$. It may, therefore, be assumed that the diffused Cu ions occupy these vacancies first and then together with other defects in the lattice (e.g. anion vacancies) form red luminescence centres. As we know (see (1)), increasing concentration of $[Cu'_{Zn}]$ lowers the concentration of cation vacancies. Therefore, after a critical concentration of the impurity is exceeded, an interstitial mechanism of diffusion begins to prevail over the vacancy mechanism.

ACKNOWLEDGEMENTS

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