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ELECTROLUMINESCENCE OF THE ZnSe M–O–S DIODES

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Injection type electroluminescence has been observed in forward biased ZnSe M–O–S diodes. The electroluminescence spectrum (emission maximum at ~ 615 nm) is due to the luminescent self-activated centres. The wavelength shifts of emission induced by voltage are discussed. The relation between the luminescence and electrical characteristics of the prepared M–O–S diodes and tentative band models are also discussed.

1. Introduction

Injecting the proper dosage of minority carriers [1–9] is a basic problem for obtaining effective electroluminescence of $A_{II}B_{VI}$ compounds. It may be carried out in heterostructures or metal-semiconductor systems (M–S) or metal-oxide-semiconductor ones (M–O–S). The present paper presents the results of investigations on electroluminescence of M–O–S diodes carried out on low resistance monocrystals of zinc selenide. The obtained results have been discussed with respect to the suggested model describing the tunneling of minority carriers through a layer of oxide to localized states [10].

2. Preparation of material for the experiments

ZnSe monocrystals of about 10 Ω cm resistivity were obtained by the high-pressure Bridgman method [11]. The crystals were oriented by means of chemical etching [12], cut along the surfaces (111) into plates about 1 mm thick and then purified in zinc by means of the Aven–Woodbure method [13].

ZnSe monocrystal plates were machine lapped and polished on both sides and then etched in a boiling 50% KOH water solution. Indium set constituted an ohmic contact. Thus the prepared surface of a sample was masked by picein and the other surface was etched in a solution of bromine in methanol. According to Allen et al. [14], this process causes the formation of a ZnO insulating layer on the etched surface.

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Gold evaporated on the insulating layer constituted the injecting electrode. The process of evaporation was carried out in a vacuum of the order of 10^{-6} Tr.

ZnSe monocrystals were not intentionally dopped, however, they can contain aluminium.

3. *Results of the measurements and their interpretation*

Fig. 1 presents the dependences of the logarithms of current and luminescence intensity on voltage (I–V and B–V) for 80 K and 300 K (the characteristics have not been corrected to series resistivity). The rectification coefficient of the obtained diodes for 2 V voltage

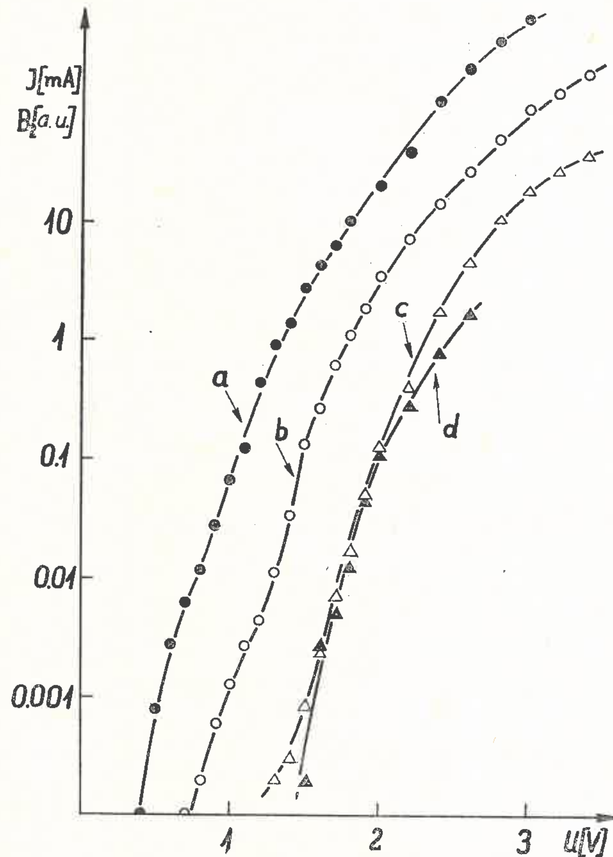

Fig. 1. Current-voltage characteristic of the diode *a* — at 300 K, *b* — at 80 K and depedence of total brightness on voltage *d* — at 300 K and *c* — at 80 K

was of the order of 10^4 both for 300 K and 80 K. Fig. 2 presents the dependence of the luminescence intensity logarithm on the current logarithm at 80 K and 300 K. The luminescence intensity *B* for low currents increased along with an increase of the intensity

current I according to the expression

$$B \sim I^{3/2}. \tag{1}$$

Higher currents followed the dependence

$$B \sim I. \tag{2}$$

The presented I–V characteristics allow one to presume that the tunnelling mechanism is crucial in the process of carrier transport. This is also indicated by a small dependence of

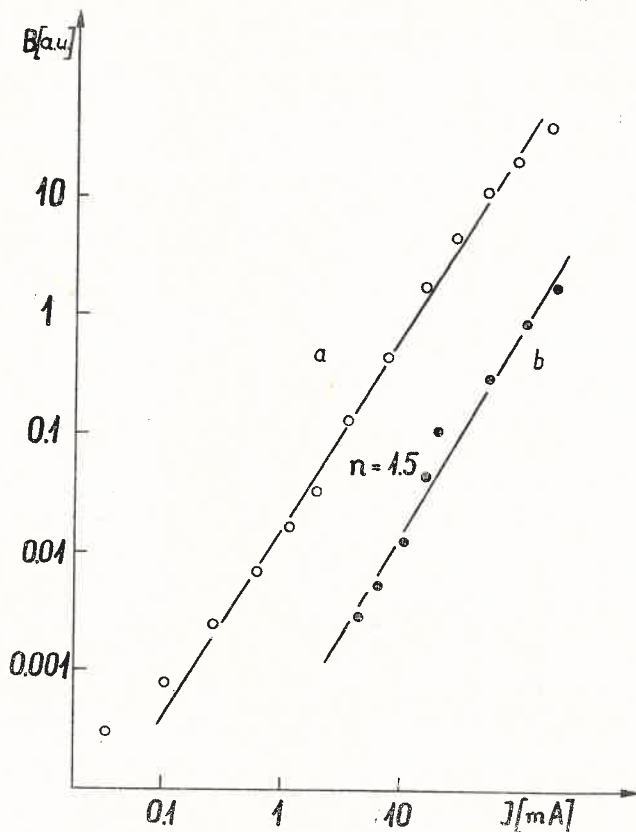

Fig. 2. Plot of brightness as a function of the intensity of the forward biased current a — at 80 K and b — at 300 K

current on temperature (almost parallel course of the a and b curves in Fig. 1) and the hump on the I–V characteristic at the moment when the process of radiative recombination begins [15–17]. Taking into consideration the following relation

$$B \sim I^{3/2} = A \cdot \exp\left(\tfrac{3}{2}\,U\right), \tag{3}$$

where A is constant, it is possible to plot the dependence of the logarithm of luminescence on voltage which is shown in Fig. 1 (c and d curves). The measured capacitance-voltage characteristics have produced no linear dependence in the system of $C^{-2} - U$ coordinates.

Similar departures from a straight line have been observed by Senechal and Basiński [18]. The estimated thickness of the junction has been lower than 500 Å. The studied diodes demonstrated electroluminescence in forward bias. Minimum voltage to make registering of luminescence possible was 1.35 V (Fig. 1). The observation of the electroluminescence process with voltage close to the threshold suggested that the light emission occured near injecting electrode.

The spectral distributions of electroluminescence of a diode, polarized in forward bias and photoluminescence of the basic material registered at 80 K by means of a system with phase-sensitive detection, are presented in Fig. 3.

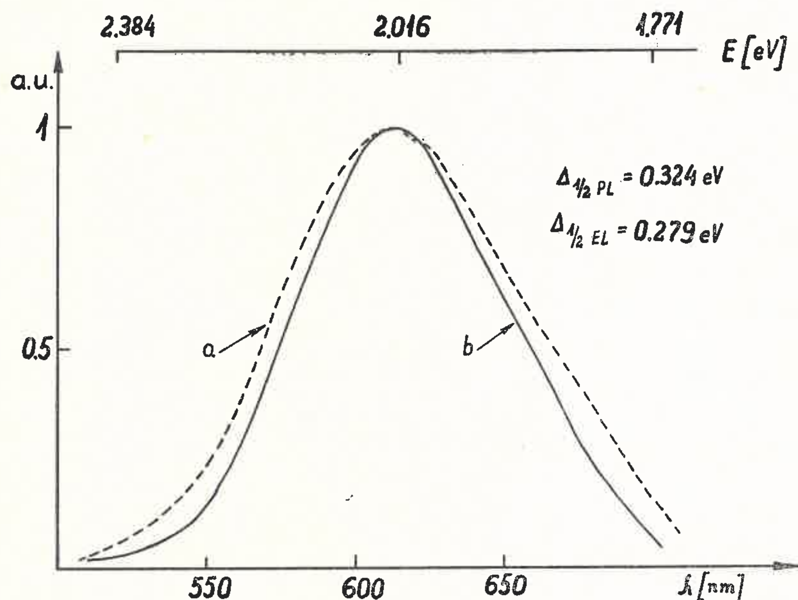

Fig. 3. Normalized spectrum distribution at 80 K; *a* — photoluminescence of the ZnSe crystal and *b* — electroluminescence of the forward bias diode with a current of $I = 4.2$ mA

The emission spectra of photoluminescence and electroluminescence ($I = 4.2$ mA) had their maxima at 615 nm (2.016 eV). The photoluminescence emission band was considerably wider than the electroluminescence band. The half-widths of photoluminescence and electroluminescence bands were $\Delta_{1/2PL} = 0.324$ eV and $\Delta_{1/2EL} = 0.279$ eV respectively. As Fig. 4 shows, the position of the maximum of the electroluminescence emission band depends on the intensity of the forward biased current in the diode. The emission maximum shifts towards the short-wave lengths along with a 0.040 eV/mA[1] increase in the current intensity. A similar phenomenon has been recorded for M–O–S type diodes made on CdS [19].

[1] From I–V characteristics in the range of the forward bias current from 2.2 mA to 7.8 mA one can find that increase 0.05 V in bias voltage causes increase 1 mA in current. From here the slope is 0.05 V/mA which is in good agreement with value 0.04 eV/mA found from the shifts of the spectra (see Fig. 4).

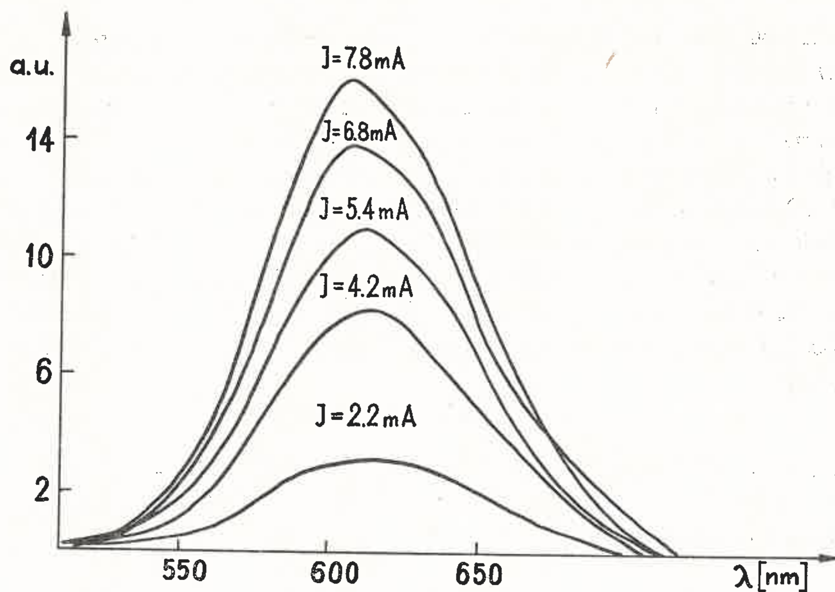

Fig. 4. Electroluminescence spectra for different currents flowing through a forward bias diode in the conductance direction. The temperature of the sample is 80 K

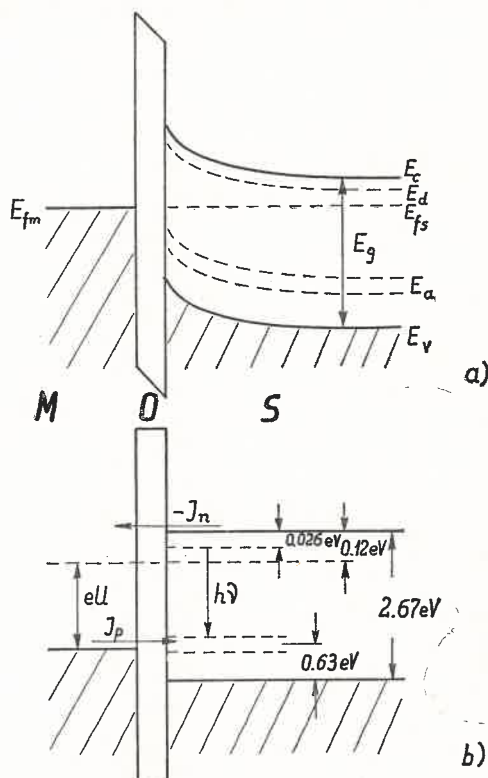

Fig. 5. Model of the process of the injection of minority carriers

This phenomenon may be explained on the basis of the model presented in Fig. 5. Under low forward biased polarization, the electrons tunnelling from the conduction band to the metal were responsible for the current. After reaching a voltage of 1.35 V there appeared, apart from the electron current I_n, the tunnel hole current I_p connected with the electron jump from the compensated acceptor levels in ZnSe and the interface states of ZnO—ZnSe to the metal. The occurrence of the hole current I_p is demonstrated by an inflection in the I–V characteristics (Fig. 1) and the appearance of electroluminescence. This electroluminescence is connected with the donor-acceptor pair recombination.

Under the forward biased polarization of the M–O–S structure, the maximum of the emission of a donor-acceptor pair should occur when the U voltage reaches the following value

$$E_{d-a} = h\nu = eU + E_{f-d}, \tag{4}$$

where E_{d-a} is the energy difference between donor and acceptor of a pair, U — voltage applied across the junction, E_{f-d} — distance of the Fermi level from the donor level. The voltage on the junction is given by

$$U = U_a - IR. \tag{5}$$

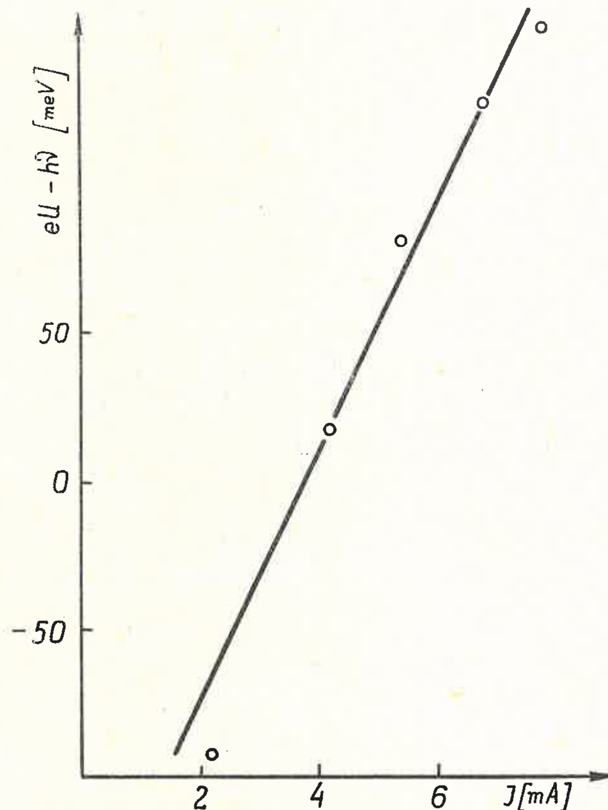

Fig. 6. Dependence of the position of emission maximum on the current flowing through a diode

where U_a is the voltage applied to the diode. The voltage value determined by the expression (4) made it possible to inject holes on compensated acceptor levels. With the increase of the voltage U, the tunnelling holes reach deeper and deeper acceptor levels which was manifested by the maximum of the emission moving towards higher energies. This dependence is shown in Fig. 6.

Using the (1), (4) and (5) formulas there was found a relationship between the luminescence intensity B and the position of the maximum of the emission [15, 20]:

$$B(h\nu) = B_0 \cdot \exp(S \cdot h\nu/e), \tag{6}$$

where $S = 40\ V^{-1}$ determined the slope of the straight line. This dependence is presented in Fig. 7.

It is interesting that the difference between the energy of photons for the maximum of the emission band and the energy of the carriers at the applied voltage of 1.9 V and

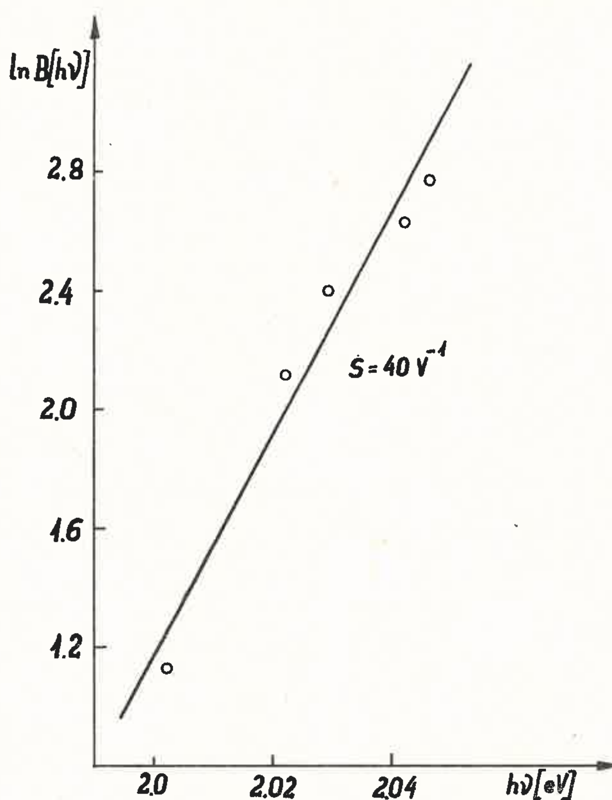

Fig. 7. Dependence of the intensity of the maximum of electroluminescence on the position of the maximum of the emission band

temperature of 80 K was 142 kT, whereas for the threshold voltage of 1.35 V it was about 850 kT. This phenomenon cannot be explained by the tail of the Boltzmann distribution and this must involve a multistep mechanism connected with tunnelling and the Auger

mechanism. Auger mechanism in *p-n* junctions has been considered by Landsberg et al. [21–23], Morgan [16] and Fischer [24].

The observed spectra of electroluminescence and photoluminescence of ZnSe (Fig. 3) characterized by wide emission bands with the maximum at 615 nm are connected with a complex consisting of a zinc vacancy and an aluminium ion [25, 26] and in the literature they are known as spectra of self-activated luminescence. This complex is formed at a high temperature during the diffusion of Al to ZnSe. This complex consists of a zinc vacancy in which one or two electrons may be trapped and of an Al impurity located at the next-neighbor sites in the ZnSe lattice. The nature of these centres responsible for the orange self-activated luminescence is not thoroughly known. Bouley et al. [27] have suggested two models of the above-mentioned centre:

a. the complex consists of a single ionized zinc vacancy and ionized Al forming a neutral defect ($V_{Zn}^{-}Al^{+}$): The luminescence may be explained on the basis of the configurational coordinate curve model [26] as a result of electron transition within that defect;

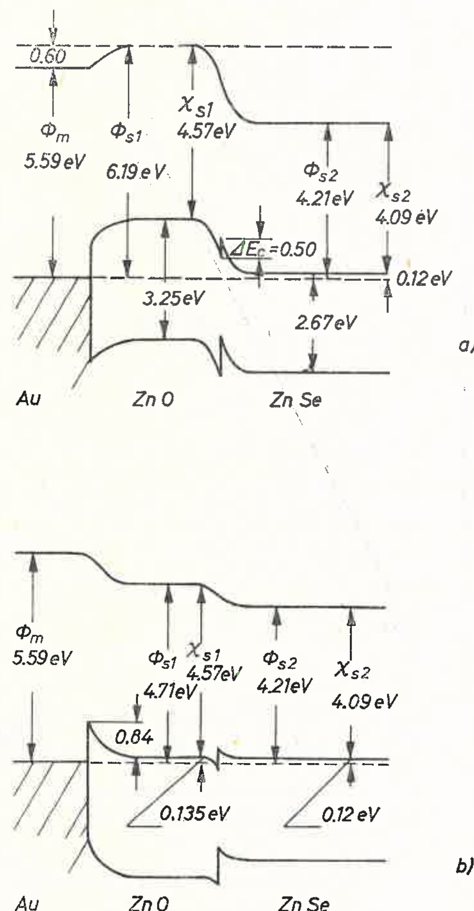

Fig. 8. Energy model of the Au–ZnO–ZnSe–In structure

b. the zinc vacancy is doubly ionized and the defect is then a singly ionized acceptor $(V_{Zn}^{-2}Al^{+})^{-}$ and a pair recombination involving an Al donor and the above described acceptor complex is responsible for the orange luminescence. The b) model seems more useful for explaining the observed spectrum of electroluminescence and photoluminescence. The recombination of the donor-acceptor pair is also supported by a displacement of the time resolved spectra (TRS) [27, 28]. The influence of the ZnO layer in the studied structure of Au-ZnO-ZnSe-In upon its properties, especially on the kind of barrier formed, has not so far been fully explained. It is known from numerous investigations that monocrystal zinc oxide is an *n*-type semiconductor of low resistivity ($\sim 0.1\ \Omega$ cm) and the depth of donor levels is 0.05 eV. It is posible to obtain high-resistance material with resistance of order of $10^4\ \Omega$ cm [29] in the form of thin layers. The layer thickness in our structure, estimated on the base of the formula (3) suggested by Livingstone et al. [14], was 200 Å. Assuming that the ZnO layer is high-resistance (insulating) and the Fermi level is situated in the middle of the forbidden gap ($E_{gZnO} = 3.25$ eV) it is possible to give an energy diagram of the structure (Fig. 8a). In the case when the material is low-resistance or degenerate (Fig. 8b) there is formed a blocking layer of the Schottky type between ZnO and ZnSe. A similar type of barrier has been recorded by Ikeda et al. [30] for Au-SnO_2-ZnSe-(In-Hg) structure where SnO_2 is degenerate *n*-type semiconductor with an energy gap of $E_g = 3.54$ eV. These authors have also stated that a diagram of C^{-2} dependence on voltage is not a straight line, which is similar to our case.

Therefore, the electroluminescence structure of Au-ZnO-ZnSe-In and especially its ZnO layer, requires further investigation.

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