METHOD OF DETERMINATION OF Mn CONCENTRATION IN ZnS BASED ON KINETIC MEASUREMENTS OF LUMINESCENCE*

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A method of determination of Mn concentration in ZnS:Mn based on existence of two manganese kinetic components is proposed. In the method the manganese concentration is determined by lifetime and initial intensity of electroluminescence measurements. The results of the measurements are compared with statistical distributions of single Mn^{2+} ions and Mn^{2+}-Mn^{2+} pairs in hexagonal ZnS.

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Introduction

Information about the dopant concentrations are very important in the field of semiconductor investigations. In many papers concentration dependences of various magnitudes are shown. In luminescence, for example, a lifetime dependence on dopant concentration is often measured [1–10]. This dependence can be used for determinaton of the dopant concentration. There are some propositions of concentration determination by optical measurements [10–12]. In the paper we propose another optical method of determination of Mn concentration in ZnS:Mn.

Description of the method

Let us assume that an activator (i.e. a dopant) creates two different kinds of monomolecular luminescent centres. Then decay curve of luminescence can be written as

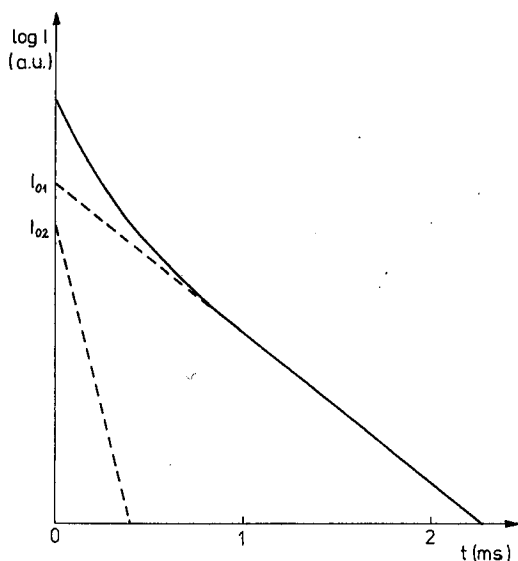$$I = I_{01} \exp(-t/\tau_1) + I_{02} \exp(-t/\tau_2), \tag{1}$$

Fig. 1.   Decay curve of luminescence in semilogarithmic scale (solid line) and its exponential components (dashed lines).

where I_0 is the initial intensity of luminescence and τ is the lifetime of luminescent centre, 1 and 2 are due to both kinds of the luminescent centres (we assume that the radiative decay of the excited centres is the dominant one). In the semilogarithmic scale, the curve can be plotted as two straight lines resulting from the presence of these two centres (Fig. 1). For a monomolecular centre, we can write

$$I_0 = \frac{N_0^*}{\tau}, \tag{2}$$

where N_0^* is the initial number of excited centres. For both kinds of the centres, we can obtain

$$\frac{N_{01}^*}{N_{02}^*} = \frac{I_{01}\tau_1}{I_{02}\tau_2}. \tag{3}$$

Assuming that the number of excited centres is proportional to the number of all the same centres in luminophor, we have

$$\frac{N_{01}^*}{N_{02}^*} = \frac{N_1}{N_2}. \tag{4}$$

It is possible to calculate theoretically probability p of finding a given kind of luminescent centres for various concentration [13, 14]. Taking into account that

$$\frac{p_1}{p_2} = \frac{N_1}{N_2}, \tag{5}$$

we obtain the following relation.
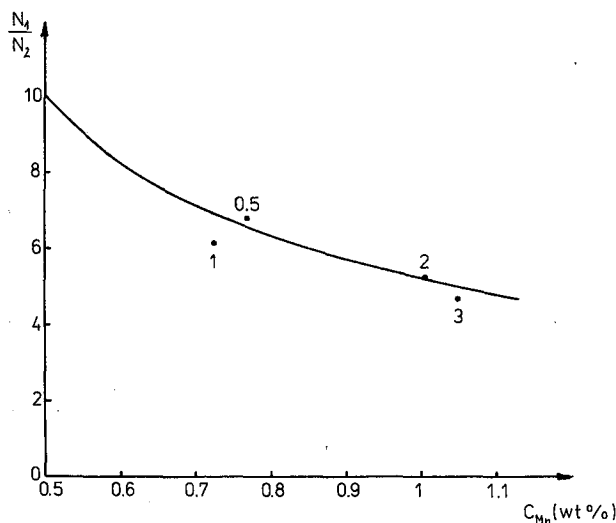
$$\frac{p_1}{p_2} = \frac{I_{01}\tau_1}{I_{02}\tau_2}.$$

(6)

Fig. 2. Ratio of number of single Mn^{2+} centres and Mn^{2+}–Mn^{2+} pairs versus Mn concentration in ZnS: theoretical curve (solid line) and experiment (points); 0.5, 1, 2, 3 wt% Mn concentration in powdered ZnS used to evaporation of the films.

Results and discussion

It is well-known that, generally, manganese in ZnS creates two kind of centres: Mn^{2+} ions and Mn^{2+}–Mn^{2+} pairs [2, 3, 7, 15]. So, we can use the above described method to determine concentration of manganese in our electroluminescent thin film cells. The preparation of the cells was described in [16, 17]. In order to determine the Mn concentration in the cells investigated, we used τ_1 the lifetime dependence on Mn^{2+} concentration introduced by Vlasenko et al. [2]. Figure 2 shows a comparison of the method described in Sec. 2 with the experiment. The solid curve represents ratio of probability of appearance of single Mn^{2+} ions and Mn^{2+}–Mn^{2+} pairs calculated from statistical distributions obtained by Behringer [13] for the hexagonal structure of ZnS matrix. As it is seen in the figure, we have obtained a satisfactory accordance between model and the experiment except point 1 (1wt%). We have not obtained a good agreement using the other data (on τ_1 vs. Mn^{2+} concentration) [1, 3–10]. Our result points out that the proposed method can be applied only when both kinds of manganese centres are excited

identically. The condition is not always fulfiled. Probability of excitation of each kind of manganese centres depends, for example, on level of excitation [18]. The method can not be also used when one kind of manganese centres are favoured during the excitation [3]. Experimental points lie over the theoretical curve when single Mn^{2+} centres are favoured and the points lie under the curve in the opposite case. In summary, the new method of determining a concentration of the dopant exhibiting two species has been proposed. We have illustrated its applicability to the situation of Mn^{2+} ions and $Mn^{2+}-Mn^{2+}$ pairs in ZnS semiconductor.

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