Effect of magnetic field on impact electroluminescence of ZnS:Mn

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Strong magnetic effects have been observed in the impact electroluminescence of ZnS:Mn films. A study has been made of these effects as a function of the temperature, the strength of the magnetic and electric fields, and the relative orientation of these fields. The experimental results are compared with the results of a theoretical analysis of various mechanisms.

An intense impact electroluminescence is observed in metal-insulator-semiconductor-insulator-metal film structures based on ZnS:Mn, which are finding progressively wider use in display screens.[1] There has been no study of the effect of a magnetic field **H** on this luminescence, despite the fact that ZnS:Mn is a semimagnetic semiconductor. In this letter we are reporting the observation and study of some strong magnetic effects in the electroluminescence of such structures.

Experiments were carried out at $T = 2$–15 K with two orientations of **H** with respect to the electric field **E**: $\mathbf{H} \| \mathbf{E}$ and $\mathbf{H} \perp \mathbf{E}$. The construction of the samples is shown schematically in Fig. 1. The Mn concentration in the ZnS:Mn film was $\approx 10^{20}$ cm^{-3}. The electroluminescence was excited by an alternating voltage u with a frequency of 5 kHz. We measured the brightness (B) of the electroluminescence, both the integral brightness and that in various spectral regions; the u dependence of the brightness (brightness-voltage characteristics); the decay kinetics of the electrolumines-

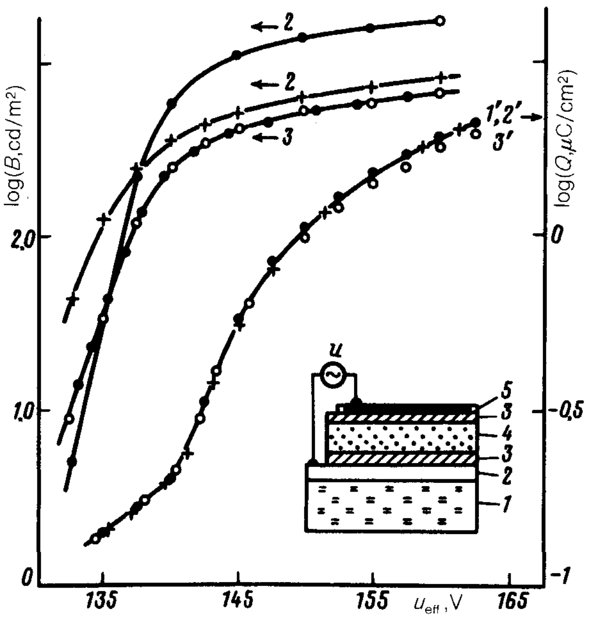

FIG. 1. Brightness-voltage characteristics (1–3) and charge-voltage characteristics (1′–3′) of structures shown schematically in the inset. 1,1′—$H = 0$; 2,2′,3,3′—$H = 4.5$ T; 2.2′—H‖E; 3,3′—H⊥E($T = 4.2$ K). 1) Substrate; 2,5) electrodes (In_2O_3 and Al); 3) insulating layers (SiO_2/Al_2O_3, 250 nm); 4) ZnS:Mn, 600 nm.

cence; and the charge (Q) which flowed through the structure over a half-period of the exciting voltage ($\tau_{1/2}$).

It was found that at $T = 4.2$ K a magnetic field causes a strong increase in B near the threshold value of u (the "positive" effect) and reduces it in the saturation region of the brightness-voltage characteristics (the "negative" effect), without affecting the spectrum or decay kinetics of the electroluminescence (Fig. 1). The positive effect is greater in the orientation H‖E, and the negative effect in the orientation H⊥E. The curve of $\log(B_H/B_0)$ versus H(B_H and B_0 are the brightness with and without a magnetic field) begins with a quadratic region, which is followed by a linear region, which in turn gives way to a sublinear region in the case of the positive effect (Fig. 2). As T is lowered, both effects are intensified; the slope of the linear region increases as $1/T$; and saturation of the positive effect begins at lower H. As T is increased to 15 K, we are left with only a small negative effect in the case H⊥E. The charge-voltage characteristic does not depend on H, within the experimental error, aside from a decrease in Q in the saturation region of the brightness-voltage characteristic in the case H⊥E (Fig. 1).

Possible mechanisms for the observed effects have been analyzed on the basis of the following representations regarding the electroluminescence.[1,2] The transition of Mn^{2+} ions from the $^6A_1$ state to the $^4T_1$ state occurs as a result of direct impact excitation by hot electrons (processes 2 and 3 in Fig. 3) or through the involvement of electron-hole pairs which arise during the impact ionization of the lattice (processes 5–11). The first of these mechanisms is predominant, especially in the initial region of the brightness-voltage characteristic. The "threshold" for the onset of electroluminescence is determined by the tunneling of electrons from deep states ($\geqslant 1$ eV) at insula-

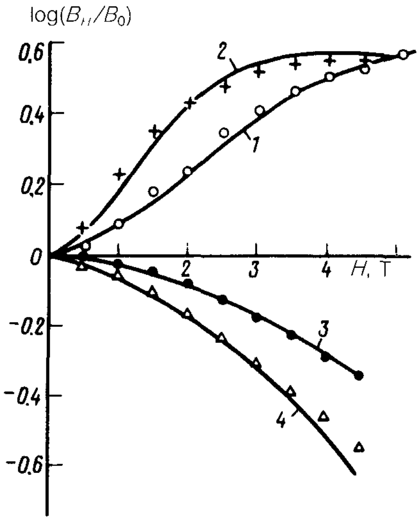

FIG. 2. Brightness versus the magnetic field in the case **H**||**E** at various values of T and u. T,K: 4,2—1.3; 2,5—2.4. $u_{\rm eff}$,V: 1,2—137; 3,4—150. The points are experimental, and the curves theoretical. 3,4) Calculated from (1); 1,2) calculated from (1) and (3).

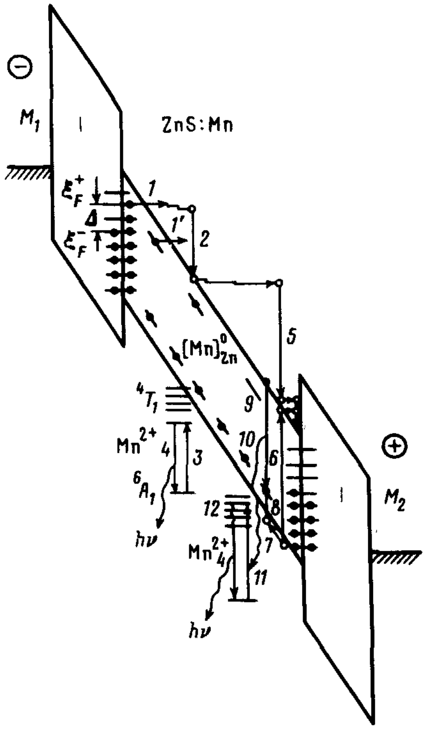

FIG. 3. Basic processing during the electroluminescence of the structures studied. 1,1'—Tunneling of electrons from surface and "bulk" levels; 2,3—direct impact excitation of Mn^{2+}; 4—radiative transition in it; 5–11—excitation of Mn^{2+} through impact ionization of the lattice, the capture of a hole by an $[\mathrm{Mn}]^0_{\mathrm{Zn}}$ defect, a recombination of it with an electron, and the resonant transfer of energy to an Mn^{2+} ion.

tor-semiconductor interfaces (process 1). The effect of the magnetic field on B might thus stem from a change in the cross section (σ_{im}) for the impact excitation of Mn^{2+} or in the changes for the generation of and/or heating of electrons.

These three mechanisms include spin-dependent processes and are based on the possibility of a polarization of the spins of conduction electrons, $P_e = -2\langle s_e \rangle$, as a result of exchange scattering by Mn^{2+} ions polarized in the field **H**. Since the Mn concentration (N) is quite high, and the cross section for exchange scattering is $\sigma_s \geqslant 10^{-16}\ \text{cm}^{-2}$, an electron may be scattered repeatedly by spins of magnetic ions over the time which it takes for one or several transits through the ZnS:Mn film. If the transit time is shorter than the spin-lattice relaxation time, and if the spin relaxation time (τ_s) for electrons trapped at insulator-semiconductor interfaces is longer than $\tau_{1/2}$ (estimates confirm that these conditions hold), then P_e will take on the value of the polarization (P_l) of neighboring sublevels of Mn^{2+} ions, which is $-\tanh(\omega_l/2T)$, where ω_l is the Zeeman splitting of the Mn^{2+} spin ($s_l = 5/2$).

The first mechanism incorporates the effect of H on σ_{im}. In a magnetic field, an increase in P_l and P_e is accompanied by an increase in the number of Mn^{2+} ions with a projection $s_{lz} = -5/2$ and an increase in the number of electrons with a spin projection of $-1/2$, which are not capable of exciting these ions to the $^4T_1$ state (because the total spin angular momentum of the Mn^{2+} ion and the electron must be conserved). A calculation of the probability for the excitation of Mn^{2+}, carried out on the basis of the equations of Ref. 3 and the fractional parentage coefficients of Ref. 4, yields the following result after an average is taken over the projections s_{lz} and s_{ez}:

$$\sigma_{\text{im}}^{(H)}/\sigma_{\text{im}}^{(0)} = \frac{3}{10}\,\frac{\sinh(2h)}{\sinh(3h)}\,[5 + 3\tanh(h)B_{3/2}(3h/2)]\,, \tag{1}$$

where $B_s(x)$ is the Brillouin function, and $h = \omega_l/T$. Since we have $B \sim \sigma_{\text{im}}$, this mechanism describes the negative effect, which does not depend on E. Calculations from (1) agree well with the experimental dependence of $\log(B_H/B_0)$ on H in the saturation region of the brightness-voltage characteristic in the case **H**$\|$**E** at the various values of T (Fig. 2).

The second mechanism, which explains the positive effect, incorporates the increase in the mean free path l and thus in the probability (α) for impact excitation which results from the weakening of the exchange scattering of electrons by the Mn^{2+} ions polarized in the field **H**. For the mean free path set exclusively by exchange scattering, l_s, the following expression has been derived:

$$l_s^{(H)}/l_s^{(0)} = [1 - P_e s B_s(\sinh)/s(s+1)]^{-1}\,, \quad s = 5/2\,. \tag{2}$$

It is difficult to calculate the functional dependence $B(H)$ for this mechanism in the absence of a theory for impact excitation in the case of a high concentration of neutral scattering impurities ($[\text{Mn}]^0_{\text{Zn}}$) and in the case of a time-varying electric field. If we use for α the expressions derived by Burraff and Keldysh (see Refs. 6 and 10 in Ref. 1), and if we assume that in addition to the exchange scattering, there is an H-independent scattering and that the condition $l_0 < l_s^{(0)}$ holds, then quantitative agreement with experiment is reached at $l_s^{(0)} < 10^{-6}$ cm. This result contradicts the standard estimate of this quantity ($l_s^{(0)} = (\sigma_s N)^{-1} \geqslant 2\times 10^{-5}$ cm).

We accordingly examined yet another mechanism for the positive effect: one based on an H dependence of the number (n) of electrons which pass through the semiconductor layer over the time $\tau_{1/2}$ and which are capable of causing an impact excitation of Mn^{2+}. The absence of a significant effect of H on Q does not rule out an H dependence of n, since Q/e might be $\gg n$ at $u \approx u_{\text{thr}}$ as a result of electrons which are tunneling from comparatively shallow "bulk" states (process 1′ in Fig. 3) and/or leakage currents along defective regions in the polycrystalline ZnS:Mn film. Analysis shows that the spin splitting of the conduction band or of the local levels in a field $H \leqslant 5$T could not strongly affect carrier generation, since the magnitude of this splitting is significantly smaller than the depth of the levels. Because of the spin polarization of conduction electrons, however, there could be a substantial difference in the quasisteady positions of the Fermi levels at the insulator-semiconductor interfaces for different spin projections ($\Delta = \epsilon_F^+ - \epsilon_F^-$). The height ($\delta$) of the potential barrier for the tunneling of electrons would then decrease by an amount $\Delta/2$ which is proportional to $P_e Q/\nu(\epsilon)$, where $\nu(\epsilon)$ is the surface-state density. Making some simplifying assumptions which are valid only near u_{thr} (charge exchange at the insulator-semiconductor interfaces does not affect E; $\nu \approx$ const in the interval Δ; and $\tau_s \gg \tau_{1/2}$), we find

$$n(H) = n(0)\cosh(C, P_e), \text{ where } C = aQ\sqrt{2m^*\delta'}/\hbar eE\nu,\ a \lesssim 1. \tag{3}$$

At $u > u_{\text{thr}}$ this problem is difficult to solve because of its self-consistent nature and its many unknown parameters. The behavior of B_H/B_0 as a function of H calculated from (1) and (3) with $C = 4.3$ and the behavior measured near u_{thr} for various values of T agree satisfactorily (Fig. 2). An estimate of ν from this value of C with $\delta \approx 1$ eV, $E = 10^{-6}$ V/cm and $\alpha \approx 1$ yields 4×10^{-12} eV$^{-1}\cdot$cm^{-2}, in agreement with estimates of this quantity by other methods.[1]

The anisotropy in the magnetic effects, which is manifested in the larger value of the negative effect in the case **H**⊥**E** and the existence of a component of the negative effect which depends weakly on T, can be explained by means of the Lorentz force, which curves the paths of the carriers and carries them into the defective surface regions of crystallites. An estimate shows that for grains with a transverse size $< 5\times 10^{-6}$ cm—this size is typical of the films studied—this mechanism could cause a decrease in not only B but also Q, as is observed in the case **H**⊥**E** and at large values of u.

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