

Title	Studies of electroluminescence on the evaporated ZnS; Cu, Mn, Cl thin film
Sub Title	
Author	佐々木, 敬介(Sasaki, Keisuke)
Publisher	慶應義塾大学藤原記念工学部
Publication year	1969
Jtitle	Proceedings of the Fujihara Memorial Faculty of Engineering Keio University (慶應義塾大学藤原記念工学部研究報告). Vol.22, No.91 (1969. ) ,p.155(7)- 157(9)
JaLC DOI	
Abstract	
Notes	Summaries of Doctoral Theses
Genre	Departmental Bulletin Paper
URL	<a href="https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00220091-0007">https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00220091-0007</a>

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## Studies of Electroluminescence on the Evaporated ZnS; Cu, Mn, Cl Thin Film

Keisuke SASAKI (佐々木 敬介)

Historically speaking, the phenomenon of electroluminescence was discovered by G. Destriau in 1936.

The invention of the transparent conducting electrode had stimulated researchers in this field from practical point of view and powder type cell was main object at that time. Recently, vacuum evaporation technique widely spreads in the field of electronics. But there are not so many investigations on thin film electroluminescence in comparison with powder type electroluminescence and, of course, emission mechanism is not yet clear. In this thesis, the author intends to establish a unified model on this thin film electroluminescence (EL) standing on collision excitation of avalanche electrons with  $Mn^{++}$  3d electrons in the so-called Schottky barrier of ZnS-Al contact.

In chapter 1, the author presents historical passage of the investigation with EL of ZnS phosphors and summarizes several remarkable results of his study and gives conclusion for them. In chapter 2 and 3, methods of sample fabrication and experimental equipments on needed characteristics are shown respectively. In chapter 4, electrical and optical characteristics are shown. Especially it is observed that electron avalanche takes place inside of backwardly biased barrier of ZnS-Al contact.

Furthermore, unipolar emission is observed when the above condition is kept. Peak of the emission spectrum is located at  $585 m\mu$  and this should be due to excited states of  $Mn^{++}$  3d electrons. Logarithm of the emission intensity against inverse

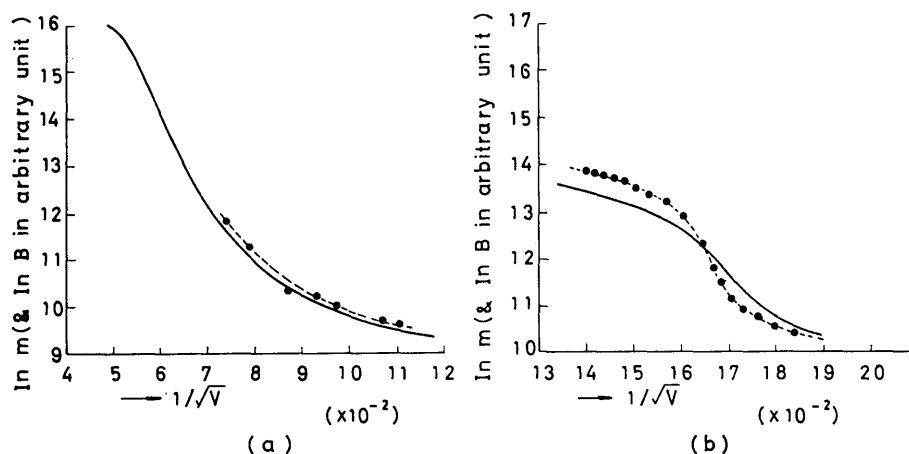


Fig. 1.

root of impressed voltage ( $1/\sqrt{V}$ ) is presented no longer by a usual linear line as in the case of the powder type cell (shown in Fig. 1 (a), (b)).

Chapter 5 is main subject of this thesis. In this chapter, the author tries to develop semi-quantitative treatment based on the experimental data with use of a simple model. In the first step of this development, it is instituted that collision excitation of  $Mn^{++}$  3d electrons with avalanche electrons in the backwardly biased barrier of ZnS-Al contact. Characteristics of the emission intensity against impressed voltage are divided into two classes as shown in Fig. 1 (a), (b).

The characteristic of Fig. 1 (a) can be explained by collision excitation of avalanche electron with  $Mn^{++}$  3d electrons with use of a simple model as shown in Fig. 2.

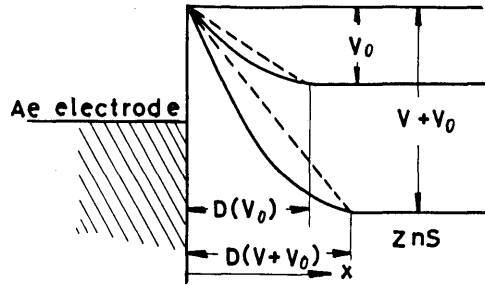


Fig. 2. The energy diagram of the Al-ZnS junction.

Effective concentration of excited luminescent centers of  $Mn^{++}$  3d electrons can be given as follows based on the above model:

$$m = M \left[ 1 - \exp \left\{ \frac{pm^*}{eH\tau_m} \sqrt{\frac{c_s \mu_0}{\alpha}} V^{-\frac{1}{2}} \exp \left( \frac{c}{\alpha \sqrt{V}} \right) \right. \right. \\ \left. \left. \times \left( 1 - \exp \left[ \frac{eH\sqrt{V}}{c_s m^* \mu_0 \alpha} \exp \left( \frac{-c}{\alpha \sqrt{V}} \right) \right] \right) \right\} \right], \quad (1)$$

$$\alpha = \sqrt{\frac{2\pi e N_0}{\epsilon_z}},$$

where symbols are as follows:

- $n$ ; electron density
- $m$ ; density of excited Mn luminescent centers
- $\mu_0$ ; electron mobility in a weak field
- $\tau_m$ ; mean free time for collision with luminescent centers
- $M$ ; density of effective luminescent centers
- $p$ ; excitation probability of luminescent centers
- $c_s$ ; velocity of sound
- $\epsilon_z$ ; dielectric constant of ZnS
- $m^*$ ; effective mass of electron

- $V$ ; impressed voltage  
 $N_0$ ; density of ionized impurities in the barrier  
 $e$ ; electronic charge  
 $c$ ; constant  
 $H$ ; correction factor

Solid line in Fig. 1 (a) is calculation of the equation (1) with suitable parameters.

Saturation of high voltage region as shown in Fig. 1 (b) can be explained by correction considering effective electric field in the barrier. This is based on the experimental fact that increase of current is definite in avalanche region of  $V-I$  curve. In other words, avalanches take place in the barrier but remaining part of the film stops infinite increase of avalanche process because of high specific resistivity of ZnS. Considering barrier voltage and potential drop of bulk region with use of multiplication factor ( $M_{ul}$ ), external voltage is given as follows:

$$V = V_b + IR = V_b + I_1 R M_{ul} V_b^{\frac{1}{2}}. \quad (2)$$

So in the equation (1), effective density of excited luminescent centers are corrected by the equation (2) and saturation of the high voltage region is explained semi-quantitatively. Also in this chapter, it is tried to explain the relation between current and emission intensity by making use of Yamashita's local equilibrium distribution function of conduction electron. Temperature dependence of emission intensity is discussed on the assumption that avalanche process is affected by optical phonon in higher temperature region and by acoustical phonon in lower temperature region respectively. The last part of this chapter is devoted to discussion and suggestion of further possibility of application from the practical point of view.

Chapter 6 is the last chapter of this thesis. In this chapter, the author summarizes essential results of this study and gives conclusion.