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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	21
page range	83-96
year	1969
URL	http://hdl.handle.net/10097/27478

Electric and Electroluminescent Properties of the Surface Layers of ZnS:Mn, Cu, Cl Films

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(Received August 15, 1969)

Synopsis

Current (I)-voltage (V) and capacitance (C)-voltage (V) characteristics of the vacuum-evaporated films of ZnS:Mn, Cu, Cl were measured. I-V curves were similar to the diode characteristics. And its cut-off voltage was about 1.1 volts. $C^{-2} \propto V$ relations also gave a diffusion potential 1.1 volts.

However, it seems that these characteristics are not due to the metal-ZnS contact but to the surface structure of films ($Cu_{2-x}S$-ZnS junction), since differences in cut-off voltage or diffusion potential were not observed either in Au or in Cu electrodes.

The band gap of the excessive Cu layer was estimated at about 1.27 eV. That is to say, an excessive Cu is thought to exist as $Cu_{2-x}S$ on the surface of ZnS:Mn, Cu, Cl films, and p-$Cu_{2-x}S$-n-ZnS heterojunctions are formed at the surface layer of ZnS:Mn, Cu, Cl films. At the forward-biased junctions, holes are injected into n-ZnS phase from p-$Cu_{2-x}S$ phase, and consequently EL emission with 580 mμ peak can be observed by Mn^{2+} which involves the energy transfer from Cu^{+} centers to Mn^{2+} centers.

EL emission localized at the anode in gap cells and EL emission in the forward-biased sandwich cells can be explained by the model of heterojunction mentioned above. On the other hand, EL emission localized at the cathode in gap cells and EL emission in the reversebiased sandwich cells under the high voltage are thought to be due to the usual mechanism of impact excitation.

I. Introduction

It has been known that additional Cu in excess of solubility of Cu (10^{-4}–10^{-3} gr. atom/mole) into ZnS had been required in order to excite the low voltage d.c EL.⁽¹⁾ However, it has not yet been confirmed, especially in the case of ZnS films in which it is still unknown where the excessive Cu exists and what role the excessive Cu plays.

Sakamoto⁽²⁾ reported that the concentration of Cu in evaporated ZnS: Pb, Cu, Cl films varied markedly toward the thickness of films. According to his results, the concentration of Cu in top of films was 2 to 2.5 times that in the rear surface of films, and the concentration of Cu in residual evaporant was 1.5 times that of Cu in the inital evaporant. Thus the top of films prepared by total evaporation is thought to include Cu of high concentration. Therefore, it is expected from the

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* Present address: College of Arts and Sciences, Tohoku University, Kawauchi, Sendai.

(1) W. Lehmann, J. Electrochem, Soc., **104** (1957), 45.

(2) H. Sakamoto, J. Electrochem, Soc., **114** (1967), 725.

solubility of Cu into ZnS and from the results reported by Sakamoto that there are somewhat an uncontinuous interface between the top and the inside of films.

In this paper, the contribution of this uncontinuous interface to the mechanism of EL under d.c low voltage were investigated by examining the electric properties and the location of EL emission in ZnS:Mn, Cu, Cl films.

II. Experimentals

II-1. Samples

ZnS: Mn, Cu, Cl films were prepared by the mixed step vacuum evaporation method.(3,4) Mixed powder of pure ZnS, $MnCl_2$ and $CuCl_2$ was fired in Ar gas at 1000°C for one hour, and it was used as evaporant. During the course of evaporation, the pressure was maintained at about 10^{-6}–10^{-5} mm Hg, and the temperature of substrate was maintained at about 200°C. Films were usually deposited to the thickness of 1–2 μ at the rate of about 0.03 gr./min. The obtained films were annealed in vacuum at 500–600°C for one hour.

There are various constructions of EL cells according to their use, but usually they are classified in two kinds, sandwich and gap type. Au, Cu and Al metals for the electrode were deposited onto the films by vacuum evaporation. The typical constructions of sandwich and gap type cell are shown in Fig. 1.

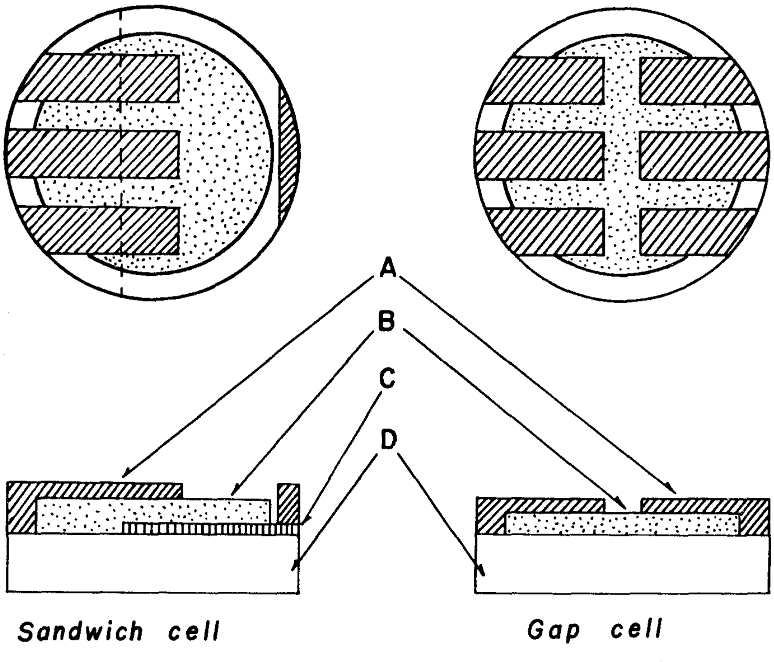

Fig. 1. Constructions of sandwich and gap cell.
A: Metal electrode B: ZnS film
C: SnO_2 conducting film D: Quartz substrate

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(3) L.R· Koller and H.D. Coghill, J. Electrochem. Soc., **107** (1960), 973.

(4) W. Uchida, H. Fujisaki and Y. Tanabe, Bull. Res. Inst. Sci. Measurements, **14** (1965), 59.

II–2. Experimental method

In measuring I-V relation, attention must be given to the electrode. The construction of sandwich cell is metal/surface layer (Cu compound)/ZnS: Mn, Cu, Cl/SnO_2 conducting film. Since ZnS film/SnO_2 contact is believed to be ohmic,⁽⁵⁾ attention must be paid to the part of metal/surface layer/ZnS.

It seems that the surface layer/ZnS interface plays the principal role, because no differences are observed between electrodes of various metals. The height of potential barrier in this interface can be estimated from the cut-off voltage. Moreover, we can obtain useful information of diffusion potential, barrier width and concentration of carriers near the barrier by measuring the capacitance and voltage dependence of the capacitance of barrier.

In measurements, electric power was supplied by dry cells and current was measured by TR–8641 μA meter. The capacitance of barrier and voltage dependence of the capacitance were measured by YHP 4206A universal bridge after the sample was allowed to stand for an hour in the dark.

Microscopic observations of EL emission in gap cells were made performed at several tens of magnification.

II–3. Results

II–3–1. I-V relation

Fig. 2 shows a typical I-V curves for the junction. It resembles the characteristics of diode except the case of Al electrode. Anomalous behaviour of cells with Al electrode is thought to result from the formation of Al_2O_3 insulting films.(5,6) Forward current flows from the metal of ZnS film, and increases exponentially as the applied voltage increases to about 2 volts, beyond which it is reduced to linear by the effect of voltage drop due to a series resistance components of ZnS films. By extraporating the linear part to the voltage axis, cut-off voltage of 1.0 to 1.2 volts was obtained in almost all samples.

Reverse current increases very slowly, but begins to increase abruptly at several tens of volts and becomes unstable. This phenomenon can be explained by means of the breakdown of ZnS films. In the gap cells, only reverse characteristics mentioned above were observed, since the gap cells have a symmetrical junction at the both electrodes.

II–3–2. C-V relation

The capacitance of junction barriers was fairly large, namely, 0.1 $\mu F/cm^2$ at 1 kc/sec under zero bias voltage. Fig. 3 shows C-V relations. C is proportional to $-1/2$ power of the voltage in the direction of reverse bias. But in the forward biased range a linearity breaks. This is considered to be due to the fact that the

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(5) P. Goldberg and J.W. Nickerson, J. appl. Phys., **34** (1963), 1601.

(6) T. Soeya, Jap. J. appl. Phys., **6** (1967), 205.

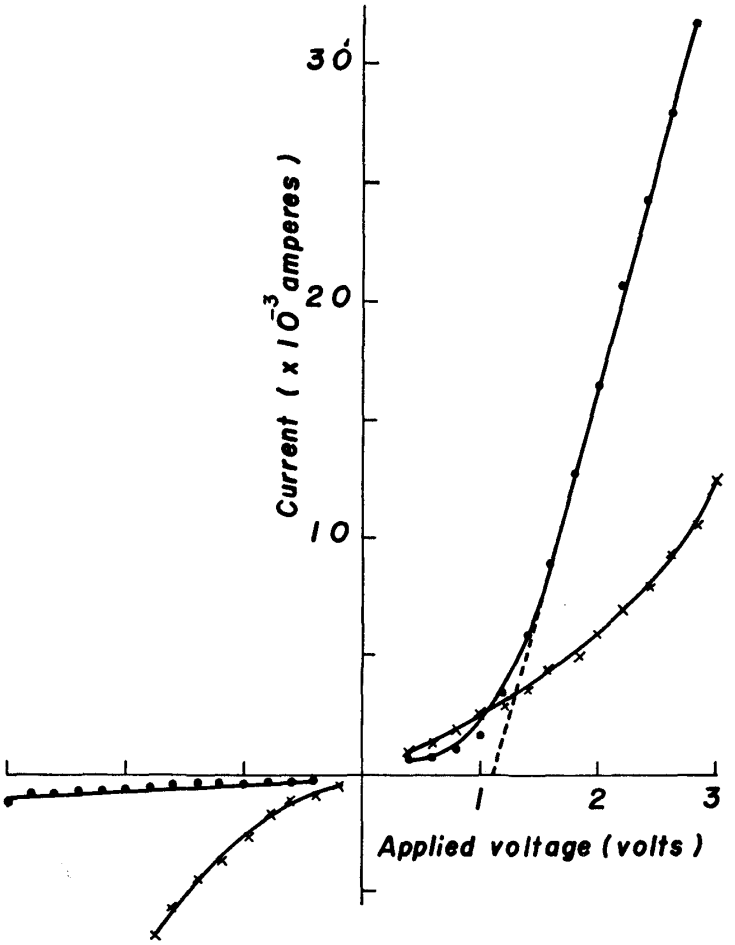

Fig. 2. Current-voltage characteristics of sandwich cells of ZnS:Mn,Cu,Cl films.
—•— : Au electrode, —×— : Al electrode.

height of diffusion potential is dependent upon the applied voltage or that the charge distribution in barrier is not constant toward the direction of thickness. Fig 4 shows the replotted curves of C^{-2} vs V. On extraporating to the voltage axis the linear part for reverse biased range, we had 1.0 to 1.2 volts as diffusion potential. This values are in good agreement with the cut-off voltage obtained from I-V relation. Differences of C were not observed between Au and Cu electrodes as well as in I-V characteristics.

The experimental results were analized, assuming the excessive Cu layer ($Cu_{2-x}S$) as many investigators did.(5,7,8) The capacitance of junction barrier per unit area can be calculated if the concentration of donors and acceptors in the n- and p-type space charge regions is respectively known. $Cu_{2-x}S$ is p-type semiconductor and forms the p-n heterojunction for the n-type ZnS. The band gap of ZnS is two times that of $Cu_{2-x}S$ and the resistivity of ZnS: Mn, Cu, Cl films is

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(7) W.A. Thornton, J. Electrochem. Soc., **108** (1961), 636.

(8) A.N. Georgobiani, "Sovet Researches on Luminescence" Transactions (Trudy) of the P.N. Levedov Physics Institute, Vol. XXIII.

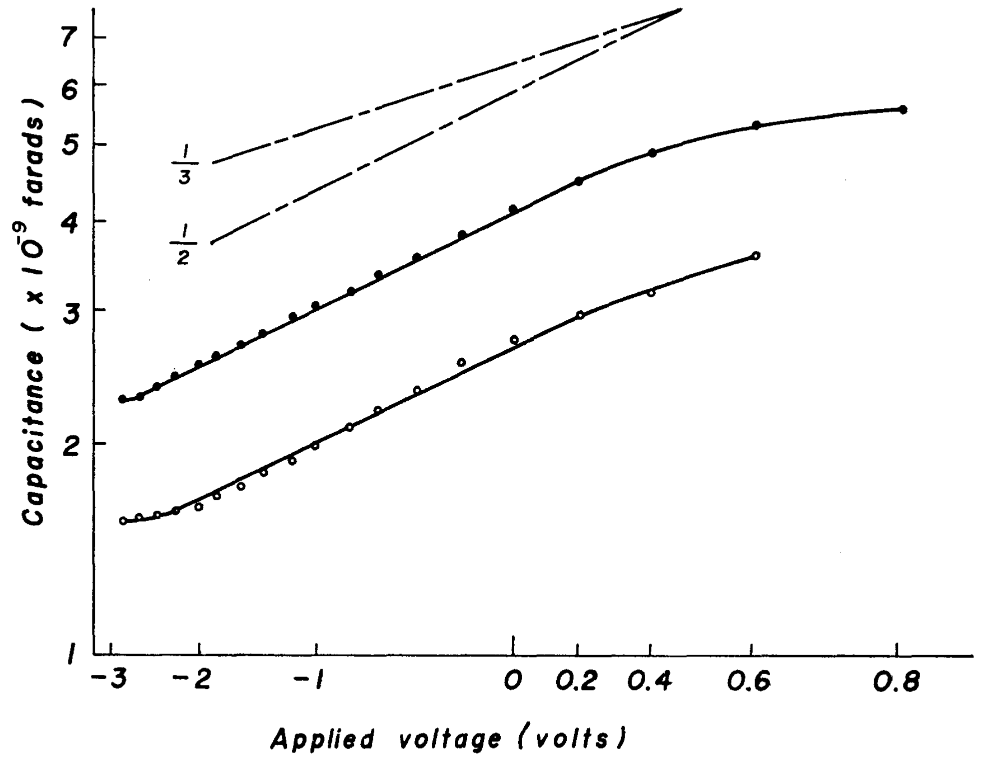

Fig. 3. Capacitance-voltage characteristics of sandwich cells of ZnS:Mn, Cu, Cl films at 1 kc/sec.

—•— : Au electrode, —o— : Cu electrode.

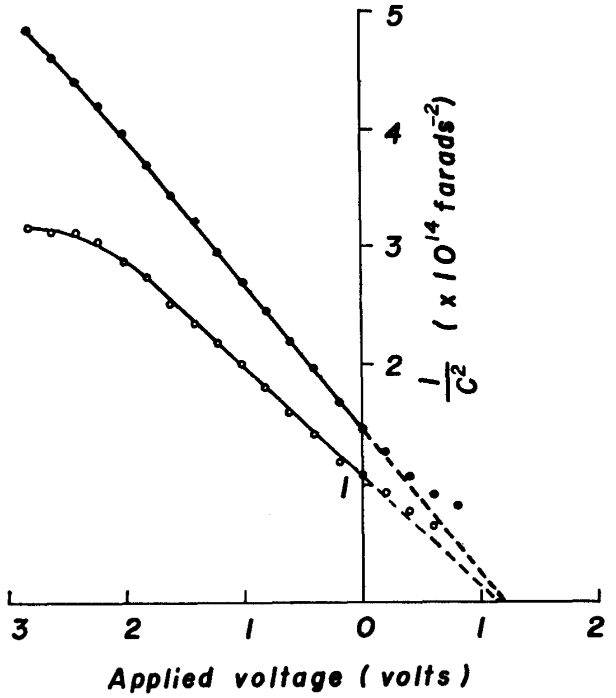

Fig. 4. The replotted curves of C^{-2} vsV from Fig. 3.

—•— : Au electrode, —o— : Cu electrode.

also as several orders larger than that of $Cu_{2-x}S$. Therefore, nearly all the bias voltages will be applied to ZnS side, and the junction barrier will be not symmetrical. That is to say, the barrier width W can be approximated as follows:

$$W \doteqdot 1.05 \times 10^{-6}\left\{\frac{\varepsilon (V_0 - V)}{2\pi e N_d}\right\}^{1/2} \qquad \text{(cm)} \qquad (1)$$

Therefore, the capacitance C becomes

$$C = \frac{\varepsilon}{4\pi W} \doteqdot 1.05\left\{\frac{\varepsilon N_d e}{8\pi (V_0 - V)}\right\}^{1/2} \qquad (\mu\text{F/cm}^2) \qquad (2)$$

From the resalts of C-V relation, the barrier width W and the concentration of noncompensated donors N_d can be estimated at $W=0.1\,\mu$ and $N_d=10^{17}/\text{cm}^3$ by using the formula (2) and the value 8.5 as dielectric constant of ZnS films.(9)

II-3-3. Brightness (B)-current(I) characteristics and others

Fig. 5 shows a typical B-I relation. The brightness of EL in the ZnS: Mn, Cu, Cl fims is proportional to n powers of current and n is about 3/2 to 2. These results are in good agreement with the values obtained by other workers.(7,10) The proportional relationship between brightness and current is apt to be thought as a characteristics of EL attributed to the injection of minority carriers. However, from the above statement a direct conclusion cannot always be obtained, although a proportional relationship may be naturally expected as a result from the injection of minority carriers.

In order to examine a close relevancy between brightness and current, temperature dependences of brightness and current were measured. Results are shown in Fig. 6. Temperature dependences of brightness and current exhibit the same appearance. From these results, it may be possible to speculate the close relevancy between brightness and current.

II-3-4. Microscopic observation of EL in gap cells

Since the intensity of EL emission is conspicuously weak, there are little studies by the microscopic observation of EL emission in ZnS films. Up to the present, there are only two reports by Goldberg and Nickerson(5) and by Soeya.(11). No coments were made in either case with respect to the relationship between gap and sandwich cells.

In the previous paper, the author(12) reported that EL emission was observed under high voltage in either case in which the metal electrode in sandwich cells was positive or negative. In the present work, the author informs that EL emission can

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(9) K.L. Chopra, J. appl. Phys., **36** (1965), 655.

(10) M. Aven and D.A. Cusano, J. appl. Phys., **35** (1964), 606.

(11) T. Soeya and Y. Kimura, Jap. J. appl. Phys., **5** (1966), 838.

(12) W. Uchida, Jap. J. appl. Phys., **7** (1968), 378.

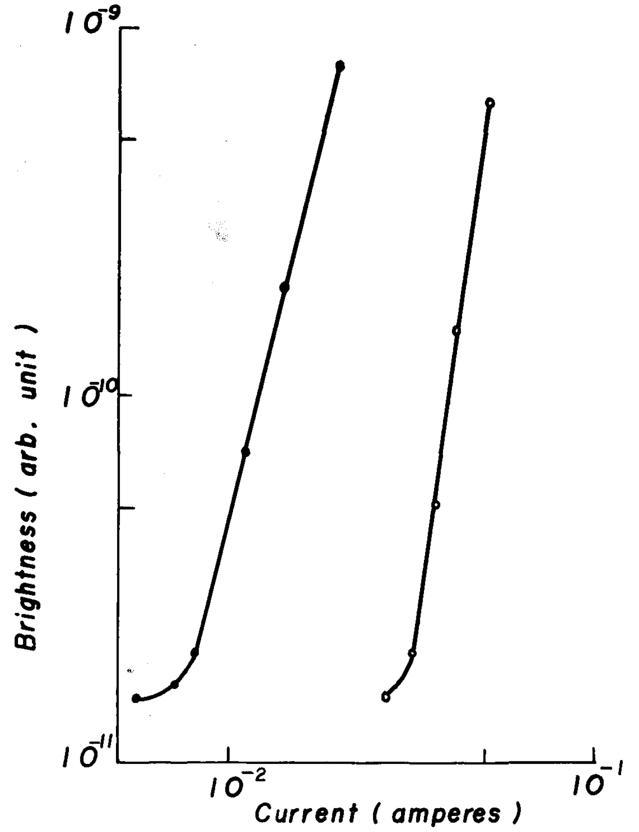

Fig. 5. EL brightness-current characteristics of sandwich cells of ZnS:Mn, Cu, Cl films.
—•— : Au electrode, —○— : Cu electrode.

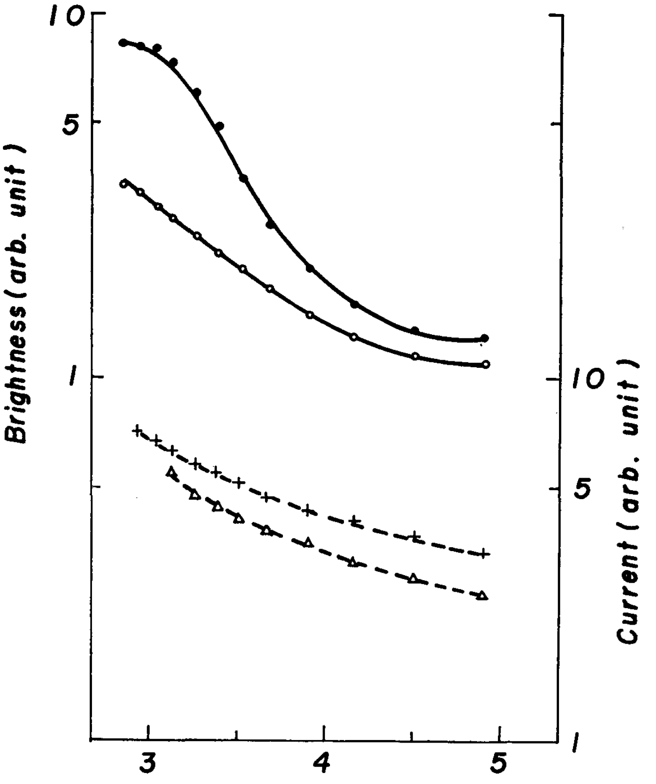

Fig. 6. Temperature dependence of EL brightness and current in sandwich cells of ZnS: Mn, Cu, Cl films. Solid lines are brightness and dotted lines are current.

be observed at the both edges of electrodes in gap cell under the fairly high d. c voltage, but before dielectric breakdown.

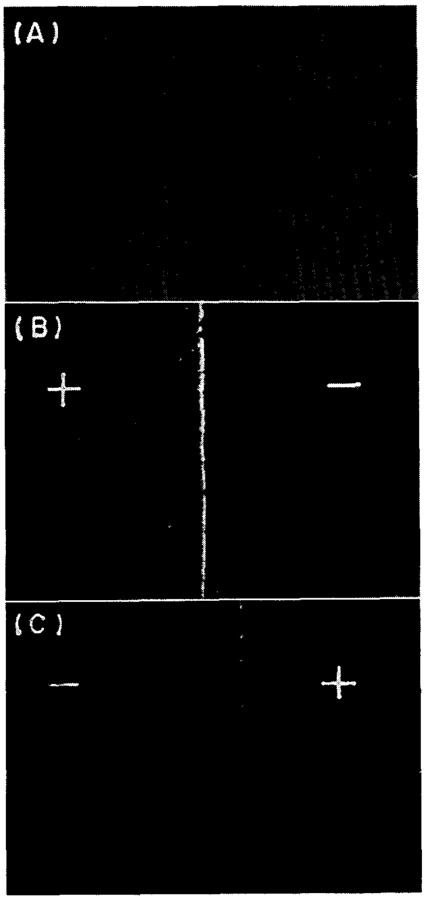

Fig. 7.

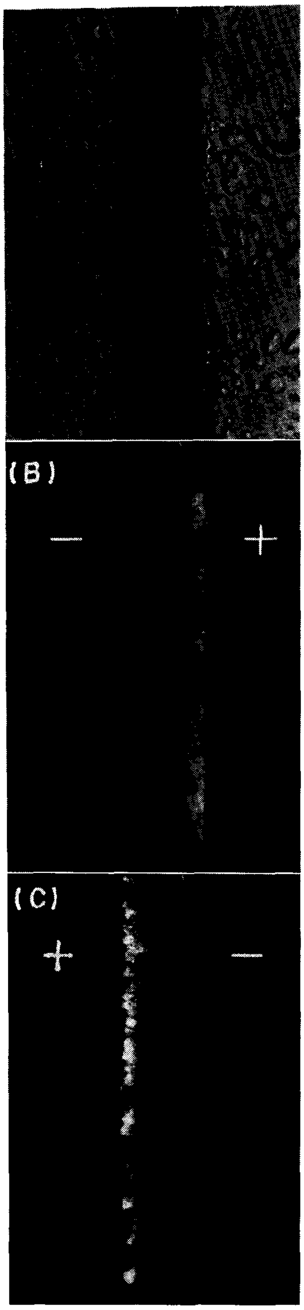

Fig. 8.

Fig. 7. EL emission along the anode of gap cell of ZnS:Mn, Cu, Cl films under the low d.c voltage.

(A) Cu electrode, about 60μ gap widths.
(B) EL emission localized at the anode, 8 volts d.c applied.
(C) EL emission localized at the new anode after the polarity reversal.

Fig. 8. Extended EL emission toward the cathode starting from the anode of gap cell of ZnS:Mn, Cu, Cl films.

(A) Au electrode, about 130μ gap widths.
(B) 18 volts d.c applied.
(C) After the polarity reversal.

Fig. 7 shows a microscopic photograph of EL emission in the gap cells of ZnS: Mn, Cu, Cl films under d. c low voltage. Emission is seen at the anode in Fig. 6 (B). On the polarity reversal of applied voltage, the position of emission moves to the new anode as shown in Fig. 7 (C). Emission at the anode thus appears under the excitation voltage of several volts. And there are a few cases where emission extends toward the cathode starting from the anode edge as shown in Fig. 8(B) and (C). This phenomenon is similar to the observation in CdS gap cell by Smith.[13]

When the applied voltage increases up to tens of volts, slight emission appears at the cathode edge together with the increase of emission intensity at the anode as shown in Fig. 9 (B) and (C).

The same phenomena were observed in the sandwich cells under the excitation of 1 kc/sec sinusoidal a.c voltage as shown in Fig. 10. Under the excitation of low voltage, an emission peak was observed in the course of a cycle when the metal

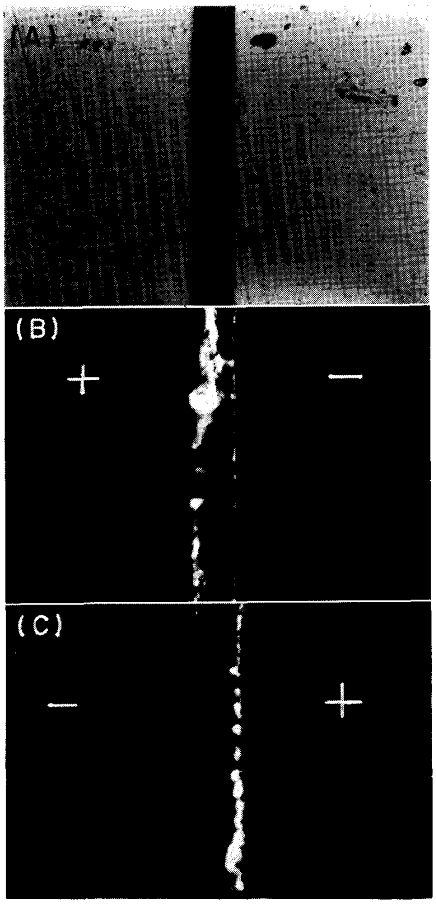

Fig. 9. EL emisson along the both electrodes of gap cell of ZnS:Mn,Cu,Cl films under the high d.c voltage.
(A) Au eleotrode, about 65μ gap widths.
(B) 40 volts d.c applied.
(C) After the polarity reversal.

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(13) R.W. Smith, Phys. Rev., **105** (1957), 900.

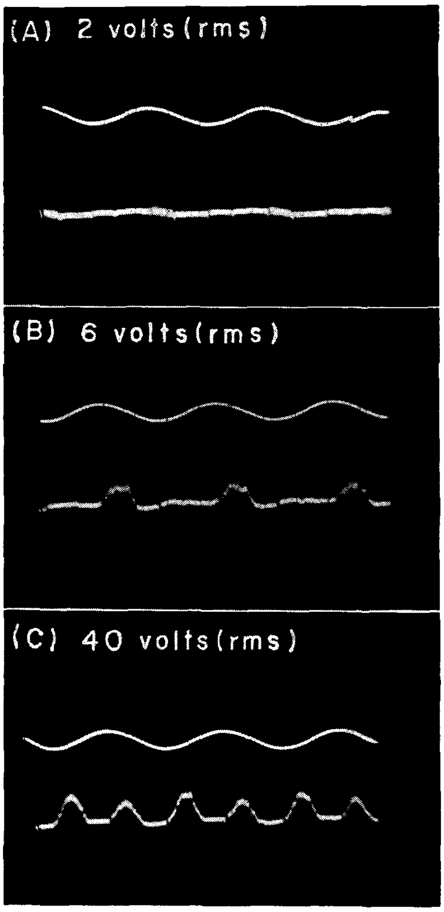

Fig. 10. The waveforms of excitation voltage and EL emission in sandwich cell of ZnS:Mn, Cu, Cl, films under the a.c 1kc/sec sinusoidal voltage. (Vartical direction is normalized)
(A) 2 volts a.c applied.
(B) 6 volts a.c applied.
(C) 40 volts a.c applied.

electrode is positive as shown in Fig. 10 (B). When the applied voltage increased, two emission peaks appeared in the course of a cycle as shown in Fig. 10(C). That is to say, emission appears even at the reverse biased junction when the applied voltage exceeds a certain threshold value.

These results suggest that the same mechanism acts in both gap and sandwich cells. The phase delay of emission peaks for the voltage peaks may be attributed to the phase delay of current for voltage.

II-3-5. Spectral distribution of EL

Fig. 11 is microphotometric spectrographs of d.c EL and PL in the ZnS films. (A), (B) and (C) films contain about 0.5 weight % Mn and 0.5 weight % Cu as activators. (A) and (B) are spectral curves of EL emission under the excitation of d. c field in the sandwich and gap cells respectively. (C) is a spectral curve of PL emission under the excitation of U.V light (365 $m\mu$). (A), (B) and (C) curves have an emission peak by Mn^{2+} in the vicinity of 580 $m\mu$ regardless of the existence of Cu

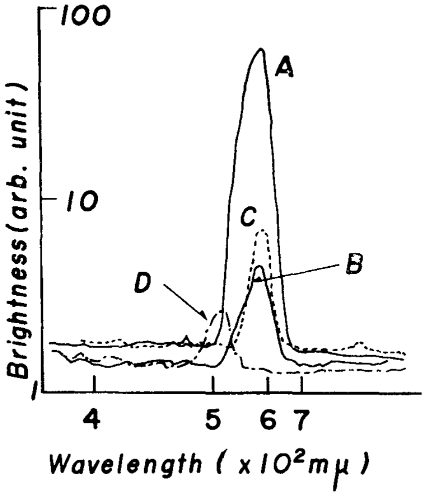

Fig. 11. Spectral distribution of d.c EL and PL emission.
(A) EL under 35 volts d.c in sandwich cell of ZnS:Mn, Cu, Cl films.
(B) EL 〃 〃 in gap cell of 〃 〃 .
(C) PL under the excitation of U.V light (365mμ) in ZnS:Mn, Cu, Cl film.
(D) EL under 35 volts d.c in gap cell of ZnS:Mn,Cu,Cl films.

activator. On the other hand, (D) film with only Cu activator exhibited EL emission with a maximum peak by Cu^+ in the vicinity of 520mμ. The films activated with Mn alone exhibited little EL and PL emission. On adding Cu (0.1 to 0.75 weight %) besides Mn to the films, EL and PL of 580 mμ are enormously emphasized by Cu associated with essential Mn activator.(14)

Spectral distribution of d. c EL in ZnS: Mn, Cu, Cl films were reported by Goldberg and Nickerson(5). Their results showed emission band with two peaks (570–575 mμ and 605 mμ), and there was a pronounced difference between the powder embeded in the castor oil and films prepared from its powder. Results in the present work does not agree with their results.

III. Discussion

Excitation mechanism of EL is roughly classified into three models:

(1) Direct excitation by the electric field.
(2) Impact excitation by the electrons accelerated in the strong field.
(3) Injection of minority carriers through the p-n homojunction or p-n heterojunction.

In the case of (1), the strength of electric field 2×10^7 volts/cm was found to be necessary in order to excite the Cu centers in ZnS by Piper and Williams.(15) However, since this value exceeds by far the breakdown field of ZnS ($2\text{–}3\times10^6$ volts/cm), there will be little chance of direct excitation.

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(14) S. Shionoya, *Luminescence of Inorganic Solids*, Academic Press, New York (1967), p. 273.

(15) W.W. Piper and F.E. Williams, *Solid State Physics*, Vol. 6 (1958) Academic Press, p. 119

The mechanism of impact excitation in (2) and injection of minority carriers in (3) are promising for EL of the ZnS films. The mechanism of impact excitation is based on the notion of electric discharge of gases. If conduction electrons traverse a path X in an electric field E, they have the energy $\Delta\mathcal{E}=\mathrm{EXe}$ and excite the luminescent centers by impact on them. Therefore, $\Delta\mathcal{E}$ must be larger than the energy of EL emission (practically, it is said that $\Delta\mathcal{E}$ requires at least 1.5 times energy of emission, when $m_e=m_p$ and the spherical structure of energy band is presumed(16)). EL spectra of ZnS: Mn, Cu, Cl films have a peak in the vicinity of 580 mμ (2.1 eV) as shown in Fig. 10. The threshold voltage in the mechanism of impact exictation is 2.1 volts at the best condition. Generally, the width of acceleration region on which the entire applied voltage concentrates is not always in agreement with the mean free path of electrons. It is said, for example, that the mean free path of conduction electrons in ZnS is 10 to 100 Å(17) and the barrier width is 100 Å to several microns.(18) On the contrary, EL emission was observed under the excitation of 2 volts d. c, as done by Thornton(19) and Goldberg and Nickerson.

Principal observations in the present works are summarized as follows:

(1) I-V characteristics is analogous to one of diode and the forward direction of current is from metal to ZnS films.
(2) C-V relation obeys $C^{-2}\propto V$ which suggests the abrupt junction. The width and height of the barrier were estimated at about 0.1 μ and 1.1 eV respectively.
(3) When the d. c low voltage with the forward direction was applied to the junction, EL emission was observed at the anode. As the applied voltage increased, anode emission became stronger and also emission appeared at the cathode.
(4) Under the application of 2 volts d. c onto the sandwich cells, EL emission was observed.
(5) Emission intensity of forward biased sandwich cell was proportional to 3/2–2 powers of current.
(6) Temperature dependence of emission intensity quite resembled one of current.
(7) Spectral distribution for EL of the ZnS: Mn, Cu, Cl films have an emission peak at the vicinity of 580 mμ by Mn^{2+} regardless of the existence of Cu activators. On the other hand, films with only Cu activator exhibited EL emission with a maximum peak in the vicinity of 520 mμ by Cu^{+}.

We have not yet succeeded in forming p-type ZnS, therefore, almost ZnS have n-type conductivity. The formation of ohmic contact at ZnS is said to be very difficult, because the electron affinity of ZnS is markedly small (=3 eV)(20,21) On

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(16) W.W. Piper and F.E. Williams, ditto, p. 10.

(17) A.N.G. Georgobiani, J. appl. Phys., **35** (1964), 197.

(18) H.K. Henisch, *Electroluminescence* Pergamon Press, (1962) p. 69.

(19) W.A. Thornton: Phys. Rev., **122** (1961), 58.

(20) G.H. Bount, M.W. Fisher, R.G. Morrison and R.H. Bube, J. Electrochem. Soc., **113** (1966), 690.

(21) A.M. Goodman: J. appl. Phys., **35** (1964), 573.

other words, rectification properties appear and the forward direction of current is from metal to ZnS. These facts agree with the experimental result (1) so long as the direction of rectification is concerned. However, it is doubtful that any differences were not observed between Au and Cu electrodes. Since discrepancies between the work function of Cu (4.52 eV) and Au (4.7 eV) are about 0.2 eV, these differences ought to appear in the cut-off voltage or the diffusion potential of barrier.

Results (3) and (4) cannot be explained by the impact excitation model. When the impact excitation mechanism is applied to the EL at the junction, emission must originate from the cathode biased reversely(11). The front paragraph of result (3), as mentioned formerly, is a fatal evidence against the impact excitation mechanism.

From these results, the low voltage EL at the forward biased junction in ZnS: Mn, Cu, Cl films seems to be attributed to the injection of minority carriers. There are two models for the injection of minority carriers; the one is the model of series of p-n junction by Thornton(7) and the other is the p-n heterojunction model which appears near the surface of films by Goldberg and Nickerson(5). Experimental results support the latter except the spectral distribution and the emission at the cathode under the excitation by high d. c voltage. Thornton reported that the number of active forward-biased junctions was about 15 per micron of ZnS phosphor, and that the minority carriers were injected into ZnS phase from the Cu compound ($Cu_{2-x}S$?) through each junction. In the case mentioned above, EL emission in gap cells ought to be distributed uniformly over the entire gap region. But this is inconsistent with the results of observation (3) and (4).

After all, most experimental results can be explained skillfully by the model of p-type Cu compound/n-type ZnS heterojunction proposed by Goldberg and Nickerson. Cu compound segregated on the surface of ZnS films may be expected from the powder and single crystal phosphors to be $Cu_{2-x}S$. Studies on $Cu_{2-x}S$ itself give us many useful informations.(22,23,24) $Cu_{2-x}S$ is well known as a p-type semiconductor with the band gap of 1 to 2.3 eV according to $x=0$ to 0.2. Furthermore, the concentration of holes in $Cu_{2-x}S$ was reported to be about 10^{19} to $10^{21}/cm^3$, therefore, Fermi level seems to be located in the vicinity of 0.02 eV above the top of the valence band. On the other hand, Fermi level in the barrier can be calculated from the noncompensated donor concentration $10^{17}/cm^3$. The result gives 0.15 eV below the bottom of conduction band for ZnS. By making use of these values, it is possible to estimate the band gap of $Cu_{2-x}S$ on the surface of ZnS films, although quasiquantitatively. The band gap of $Cu_{2-x}S$ was estimated $E_b=1.1+0.15+0.02=1.27$ eV. This value is in good agreement with the data on $Cu_{2-x}S$ reported

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(22) R. Marshall and S.S. Mitra, J. appl. Phys., **36** (1965), 3882.

(23) E. Hirahara, J. Phys. Soc. Japan, **6** (1951), 428.

(24) N. Nakayama, J. Phys. Soc. Japan, **25** (1968), 290.

Marshall.(22) Finally, it may be concluded that the excessive Cu is segregated on the surface of ZnS: Mn, Cu, Cl films and form $Cu_{2-x}S$.

IV. Conclusion

In order to excite EL in ZnS: Mn, Cu, Cl films under d. c low voltage, Cu of high concentration is required in excess of the solubility of Cu into ZnS phosphors as well as in ZnS powder and single crystal. This excessive Cu is segregated in the form of $Cu_{2-x}S$ on the surface of film, and $Cu_{2-x}S$ plays a important role in an injection of holes into ZnS phase. The existence of $Cu_{2-x}S$ on the surface of ZnS: Mn, Cu, Cl film was confirmed by means of some electrical properties and EL emission under d. c low voltage. Furthermore, an evidence based on the structure analysis (for example, by electron diffraction) is desired.

Acknowledgement

The author thanks Professor Y. Tanabe and Dr. H. Fujisaki at the Research Institute for Scientific Measurements, Tohoku University for their helpful discussions and encouragement.