Abstract:

ZnS:Mn is the most efficient EL material known to date. Though ZnS based EL devices have long life and high brightness it requires a high driving voltage. In this chapter the fabrication of low voltage operated thin film EL device with novel dielectric Eu₂O₃ in MIS structure is described. TFEL devices with ZnS:Mn as active layer and Eu₂O₃ or MgF₂ as insulator have been found to possess a frequency dependent threshold voltage for onset of EL emission. This effect is explained on the basis of frequency dependent loss tangent of the insulating material. The device parameters of TFEL device with Eu₂O₃ as insulator is optimised in terms of thicknesses of active and insulator layers. It is observed that a thickness ratio of 1 and 2 between active and insulator is suitable for low voltage operation. TFEL devices with insulators of different figure of merit are fabricated. From the EL emission characteristics it is concluded that films with high figure of merit is suitable for low voltage operation.
5.1 Introduction

AC thin film EL (ACTFEL) devices with double insulated structure [1] are known for their long life and high brightness. They are emerging as practical flat panel display systems because of a number of attractive properties. These include low power dissipation and the possibility of fabricating large area solid state multicolour flat panel displays with integrated driving circuits. The most popular double insulated ZnS:Mn TFEL device consist of an active layer of ZnS:Mn sandwiched between two insulating layers of $Y_2O_3$. Even though they have high brightness level ($\sim 1500$ fL) and long life[2,3] ($>20,000$ hours) they require a fairly high driving voltage of about $200$ V. This makes it difficult to use them with a compact driving circuit composed of available ICs. In some practical systems this problem is solved to some extent by adding an external inductor to the device which is capacitive in nature, thereby forming an LC resonant circuit. Devices with Metal-Insulator-Semiconductor (MIS) structure have been suggested as one way of reducing the driving voltage requirements of TFEL devices [4]. Another possible approach is by incorporating dielectrics of high figure
of merit for the insulating layer. According to Howard [5] in order to obtain high brightness and high efficiency for these devices, the insulator film must satisfy the condition that the product of its dielectric constant ($\varepsilon$) and breakdown voltage ($F_b$) must be at least three times higher than the corresponding value for the active ZnS:Mn layer. This implies that low voltage operation can be obtained without sacrificing the brightness or efficiency by using insulators of high dielectric constant, and preferably, with high breakdown voltage. Based on this idea Okamoto et al. [6] have prepared a device using piezoelectric PbTiO$_3$ ($\varepsilon = 150$) insulating layer and found that they can operate at $\sim 50$ Volts. Attempts are also being made to use SrTiO$_3$ and BaTa$_2$O$_3$ films in such devices [7]. Another innovative idea on this type of devices is due to Yoshiro Oishi et al. [8] and Y.A Ono et al. [9] who have very recently fabricated tunable colour EL devices.

Quite different from these attempts, as described in this chapter, the author has prepared an AC thin film EL device of ZnS:Mn having an insulator with a frequency dependent characteristics which modifies the device performance in such a way that it can be switched on and off, by changing frequency while keeping its amplitude constant.
This makes the high voltage switching unnecessary and hence minimises capacitive loading. Eu$_2$O$_3$ insulator has been used and the choice of Eu$_2$O$_3$ as insulator was motivated by the fact that it has got a dielectric constant [10] of 22 and breakdown strength 2 x 10$^6$ V/cm. However, the loss factor and hence the effective impedance vary with the applied frequency [10]. The devices were prepared in both MIS as well as MISIM structure using ZnS:Mn active layer and Eu$_2$O$_3$ as insulator. Optimisation of device parameters in terms of thickness of active and insulating layers is also dealt with in some detail in the present chapter.

The following sections of this chapter also give the details of fabrication and study of MIS and MISIM structure devices with ZnS:Mn and insulators having different figure of merit such as MgF$_2$, Sm$_2$O$_3$, CeO$_2$, SiO, Na$_3$AlF$_6$, BaTiO$_3$.

5.2 Fabrication of MISIM and MIS structure devices

The AC TFEL device with MISIM and MIS structure fabricated for the present studies is as shown in Fig. 5.1 a,b. The substrates used were 1 mm ordinary glass substrates of 7.5 cm x 2.5 cm size. All the layers
except the transparent conducting electrode were deposited by thermal evaporation. The detailed procedure for deposition of each film is given below.

The SnO$_2$ conducting films on the glass substrates were deposited by the chemical spray pyrolysis method which is described in detail in Chapter-II. For the fabrication of thin film devices, films of sheet resistance 80 Ohm/square and of transparency 85 percent were used. The deposited electrodes were then suitably etched by a chemical method. These transparent electrodes were then cleaned with soap solution and washed with water, then rinsed in distilled water, xylene and acetone successively. The plates were subjected to an ultrasonic cleaning procedure. The plates were then dried and loaded into the coating chamber.

For the deposition of the layers in the device of the type SnO$_2$- Eu$_2$O$_3$-ZnS:Mn-Eu$_2$O$_3$-Al and SnO$_2$-ZnS:Mn-Eu$_2$O$_3$-Al, weighed amounts of Eu$_2$O$_3$ and ZnS:Mn which are slightly in excess needed for the deposition of required thickness were taken in the respective source heater. For Eu$_2$O$_3$ a tungsten basket was used as source heater which was powered by a 200A, 10V transformer. The ZnS:Mn was taken in the form of pressed pellets and the source used was a molybdenum box type heater. The active layer
was obtained in the present case by evaporating electro-
luminescent ZnS:Mn phosphor having 3 wt percent of Mn
prepared in the laboratory by the slurrying technique
as described in Chapter-II. During the deposition the
substrate temperature was maintained at 423 K. The
device fabrication was completed by the deposition of
the final aluminium back electrode. This was done by
the usual vacuum evaporation method. The aluminium
film was deposited through a mica mask suitably prepared
so that on each substrate 5 electrode strips of size
1 cm x 0.5 cm were formed. This resulted in five
identical devices each of emitting area 0.5 cm.

On the first application of electric field to
a newly built cell, there occur spurious arcing and
momentary rupturing of the metal electrode followed by
the emission of light. Due to the self healing, pin
hole burn-out occurs in small isolated regions. Even-
though there exist burnt-out portions, they are not
visible when the device is switched on as the entire
area is uniformly illuminated. The cells were then
operated for several hours continuously without any
observable deterioration. To ensure reliability,
device operated for long a time duration only have
been subjected to detailed investigation. Also
Fig. 5.1. Schematic structure of (A) MISIM TFEL, and (B) MIS TFEL devices used for present investigations.

Fig. 5.2. EL emission spectra of ZnS:Mn TFEL device.
these devices even without any protection layers, can operate for months without any sign of deterioration.

The EL spectrum of TFEL cell was recorded with the set up described earlier (Chapter-II). The excitation set up and the arrangement for the voltage-brightness measurements are the same as used for the study of powder cells described in Section 2.6 of Chapter-II.

5.3 **Frequency dependent threshold voltage of the devices**

The EL emission spectrum recorded for both MISIM and MIS cells are the same and typical spectrum is shown in Fig. 5.2. The emission has its maximum at 585 nm and the width at half maximum is 40 nm. This is due to the well known intra-atomic transition of the Mn$^{2+}$ ion from $^{4}T_1$ to $^{6}A_1$ state [11]. The B-V characteristic obtained for the present devices was found to depend strongly on the excitation frequency as can be seen in Fig. 5.3 for MISIM device. The brightness is found to be zero upto a threshold voltage ($V_{th}$), beyond this value of the applied voltage the brightness increases steeply and after attaining a certain brightness value it levels off indicating saturation. Such a saturation effect has been observed for all type of AC thin film EL
devices as well as in some DC powder EL devices [12].
Tornquist [13] has attributed this apparent brightness saturation to two cases: (1) Due to the dissipative current in the ZnS:Mn layer that is directly related to the excitation of Mn$^{2+}$ ion (This is because at higher fields the conductivity of ZnS:Mn layer will increase and hence the internal field will be limited by the capacitance of the insulating layers), (2) Due to the internal quenching of Mn$^{2+}$ emission.

The device is found to have frequency dependent threshold voltage, that is the voltage for onset of EL emission increases with excitation frequency. This observation, though anomalous at first sight, can be explained on the basis of the physical properties of materials used in the fabrication of the device.

In order to understand the usual B–V characteristic of the TFEL devices an equivalent circuit as shown in Fig. 5.4 adapted by Tornqvist [13] is made use of. But in the present equivalent circuit an additional parallel resistance $R_1$ is included. The resistance $R_1$ included in the circuit accounts for the leakage currents. The voltage appearing across the active layer can be
Fig. 5.3. B-V characteristic of ZnS:Mn MISIM structure TFEL device with Eu$_2$O$_3$ insulator at different excitation frequency.

Fig. 5.4. The equivalent circuit for the TFEL device.
expressed as

\[ U = \frac{Z_s}{Z_i + Z_s} V \]  \hspace{1cm} 5.1

where \( V \) is the applied voltage, \( Z_i \) is the total impedance offered by the insulating layers and \( Z_s \) that of the active layer. \( C_i \) and \( C_s \) are the equivalent capacitance of the insulator and active layers. If \( U_{th} \) is the threshold voltage for the onset of emission and \( V_{th} \) is the corresponding applied voltage having a particular frequency \( \omega \) then

\[ U_{th} = \frac{Z_s(\omega)}{Z_i(\omega) + Z_s(\omega)} V_{th} \]  \hspace{1cm} 5.2

\( U_{th} \) is the threshold voltage to be applied across the active layer for the onset of light emission and \( V_{th} \) the corresponding applied voltage. But \( Z_i(\omega) \) will be proportional to \( R_i / V_{th} 1 + \tan^2 \delta \) which means that the voltage drop across the insulator layer is a function of \( \tan \delta \) and higher the \( \tan \delta \) value the lower the \( Z_i(\omega) \) value or drop across the insulator. So for higher \( \tan \delta \) value the \( U_{th} \) can be attained for a much lower applied voltage as is evident from equation 5.2. In the case of \( Eu_2O_3 \) its \( \tan \delta \) value is strongly dependent function of frequency and it goes on decreasing as the frequency
is increased [10]. The variation of $\tan \delta$ with frequency is given in Fig. 4.4. This leads to the result that by increasing the excitation frequency the $\tan \delta$ value is increased thereby increasing the value of the applied voltage required to produce emission from ZnS:Mn. Thus one can conclude that the threshold voltage should depend on the excitation frequency and the nature of this dependence must be as shown in Fig. 5.3.

5.4 Optimisation of device parameters

To fulfil the potential needs, a number of approaches for lowering threshold voltage have been attempted. For example, the use of lower band gap host material such as ZnSe [14], low energy Mn ion implantation into the ZnS [15], thin active and insulating layers [16], etc. have been tried so far. MIS structure devices [4] and use of dielectrics [5] of high figure of merit are also possible ways of reducing the driving voltage. Although many interesting results have been obtained, no definite practically available solution has been found.

In order to fabricate legible low-voltage driven, high brightness yellow-orange emitting ZnS:Mn TFEL devices, MIS structure as shown in Fig. 5.1b have been investigated.
The following section gives the detailed emission characteristics of ZnS:Mn MIS TFEL devices and information on the optimal conditions of the active and the insulator film thickness ratio in low-voltage driven MIS TFEL devices.

The devices in MIS structure (Fig. 5.1b) were fabricated with different active layer thickness keeping the insulator layer thickness and devices having different insulator thickness but keeping active layer thickness constant. The deposition procedure and conditions are the same as described in the case of MISIM structure devices as in Section 5.2.

Figure 5.5 shows the dependence of brightness on the thickness of the active layer in ZnS:Mn MIS TFEL device with constant insulator thickness of 0.2 µm. The brightness is found to decrease as thickness of the ZnS:Mn active layer is reduced. The threshold voltage of the device also decreased with the decrease of active layer thickness. Fig. 5.6 shows the dependence of the brightness on insulator thickness with a constant thickness of 0.3 µm for active layer. The threshold voltage again decreases with decrease of insulator layer thickness.
Fig. 5.5. Dependence of brightness on thickness of active layer in MIS structure device under 1 KHz excitation frequency.

Fig. 5.6. Dependence of brightness on insulator layer thickness in MIS structure device under 1 KHz excitation frequency.
In MIS, TFEL devices the mechanism of EL evidently is the impact excitation of the emission centers by accelerated charge carriers injected into the active layer. These carriers can originate from the electrode, ZnS-insulator interfaces, ZnS-SnO₂ interface states and also from trapping levels in ZnS layer. When ZnS (active layer) thickness is reduced, the number of emission centers correspondingly decreases and acceleration efficiency is reduced owing to low crystal quality [17,18]. This may reduce the maximum brightness with the decrease of ZnS layer thickness. Further in the case of MIS structure electron leakage to SnO₂ side is smaller, for thick layers of ZnS owing to grain boundary barriers [19] than for thin ZnS layer. On reducing the insulator thickness the number of electrons injected from the insulator side is increased. Thus reduction of insulator layer thickness helps in increasing the EL emission intensity. For thicker layer of insulator, voltage drop across the insulator is high, necessitating higher applied voltage for the onset of emission.

Figure 5.7 shows the variation of maximum brightness with ratio of active layer (ZnS) to insulator thickness \( \frac{t_z}{t_I} \). It is found that brightness increases up to a value of 1.5 for \( \frac{t_z}{t_I} \) and then begins to saturate. Curve B shows the variation of threshold voltage with \( \frac{t_z}{t_I} \). The
threshold voltage is found to increase with increase of either $t_z$ or $t_I$. From Fig. 5.7 it is clear that a thickness ratio of $t_z/t_I$ between 1 and 2 is best for low voltage operation and maximum brightness.

The driving voltage of TFEL devices can be reduced either by reducing the thickness of the active layer (ZnS) or the insulator ($\text{Eu}_2\text{O}_3$) or both. For a thicker insulator layer $Z_i(\omega)$ is high causing a decrease in the maximum brightness. When the insulator is too thin there is a possibility for breakdown. The optimal condition for high stability as well as brightness is found to be for a thickness ratio lying between one to two for the ZnS-$\text{Eu}_2\text{O}_3$ layers.

The MIS structure device also shows a frequency dependent threshold voltage for onset of emission as in the case of MISIM device. Figure 5.8 gives the variation of threshold voltage for the onset of emission for a typical cell of MIS structure with active layer (ZnS) thickness 0.3 $\mu$m and insulator ($\text{Eu}_2\text{O}_3$) thickness 0.2 $\mu$m. This can be explained in similar manner as in the case of double insulating devices.
Fig. 5.7. Variation of maximum brightness with $t_z/t_I$-curve A ( o ... o for $t_I=0.2 \mu m$, ••• for $t_z=0.3 \mu m$) and variation of $V_{th}$ with $t_z/t_I$-curve B ( o—o for $t_I=0.2 \mu m$, •• for $t_z=0.3 \mu m$)

Fig. 5.8. Variation of $V_{th}$ excitation frequency of a typical MIS TFEL device with active layer 0.3 \mu m and insulator 0.2 \mu m thickness.
5.5 \textbf{Devices with insulators having different figure of merit}

A number of approaches to lower the driving voltage have been attempted; such as using small band gap semiconductor materials, the use of insulators with high dielectric constant, etc. Although the driving voltage was reduced by such attempts, the brightness also was reduced simultaneously. The reason for this is considered to be the low resistance and the deviation from stoichiometry in the semiconducting as well as the insulating films.

Insulators with a high dielectric constant and low dielectric loss factor should be used as the TFEL insulator in order to achieve a low voltage driven high brightness TFEL device. Hence TFEL devices were fabricated in MISIM and MIS structure with ZnS:Mn active layer and insulating layers of different figure of merit such as Sm$_2$O$_3$, Eu$_2$O$_3$, MgF$_2$, Na$_3$AlF$_6$ and CeO$_2$. In the following section the details of fabrication and emission characteristics of the devices are given.

All the devices prepared have the same emitting area of 0.5 cm$^2$. In the case of MISIM structure devices (Fig. 5.1a) the thickness of insulator was 0.3 μm and
that of ZnS:Mn was 0.6 μm; whereas in the case of MIS structure (Fig. 5.2b) the thickness of insulator was 0.2 μm and that of the active layer was 0.3 μm. All the devices were prepared by vacuum evaporation of each layer sequentially using electron beam gun in single pump down cycle. During the deposition of the insulator and active layer the substrate temperature was maintained at 150°C and annealed for 1 hour after each layer deposition. But in the case of devices with MgF₂ and Na₃AlF₆ the higher substrate temperature and the subsequent annealing actually diminished the emission. However, in the case of Eu₂O₃ and Sm₂O₃, CeO₂, SiO insulating devices, the annealing and higher substrate temperature improved the device quality. This is mainly because of the improvement of dielectric properties of insulating film as we have seen in Chapter-IV, and not contributed by ZnS:Mn active layer. This observation is supported by the recent studies on Y₂O₃ insulator devices by Theis et al. [20] with the aid of transmission electron microscopy. However, during deposition of ZnS:Mn the substrate temperature is found to increase. So in the case of MgF₂ and Na₃AlF₆ insulating devices the substrate temperature was maintained at about 80°C. Compared to other insulators MgF₂ and Na₃AlF₆ are highly sensitive to moisture. Hence protection layer is necessary for these
The TFEL device with MgF$_2$ and Eu$_2$O$_3$ as insulating layer are found to exhibit a frequency dependent threshold voltage for onset of emission. The B-V characteristic of Eu$_2$O$_3$ device is shown in Fig. 5.3, and that of MgF$_2$ insulating device is given in Fig. 5.9. The reason for this can be explained in terms of frequency dependent loss factor of the insulating film (see Section 5.3). The loss factor of MgF$_2$ film is found to decrease with increase of frequency [21] as shown in Fig. 4.21. The explanation given for Eu$_2$O$_3$ insulating film holds good in the case of MgF$_2$ insulating devices also.

The EL emission spectrum of all the devices are the same as those of conventional ITO-Y$_2$O$_3$-ZnS:Mn-Y$_2$O$_3$-Al. The typical EL emission spectrum is given in Fig. 5.2.

Figure 5.10 shows the brightness-voltage (B-V) characteristic of MISIM devices having an active layer thickness 0.6 µm and insulator layer thickness of 0.3 µm excited under 1 KHz excitation frequency. Fig. 5.11 gives the B-V characteristic of the MIS devices with active layer thickness of 0.3 µm and an insulator thickness of 0.2 µm. It is observed that the threshold voltage for onset of emission is minimum for devices.
Fig. 5.9. B-V characteristic of ZnS:Mn MIS TFEL device with MgF$_2$ as insulator at different excitation frequency.

Fig. 5.10. B-V characteristic of MISIM TFEL device under 1 KHz excitation frequency. (ZnS: Mn - 0.6µm and insulator 0.3 µm)
Fig. 5.11. B-V characteristics of MIS TFEL devices under 1 KHz excitation (ZnS:Mn - 0.3 µm and insulator 0.2 µm).
with $\text{Sm}_2\text{O}_3$ insulator. Table 5.1 illustrates the insulator material used in TFEL device with the value of its dielectric constant and loss factor (at 1 kHz) at room temperature. It also gives the breakdown strength of the insulator material and the threshold voltage for onset of emission for MISIM and MIS structure based devices at 1 KHz excitation frequency.

The threshold voltage for onset of emission is minimum for the device with insulator $\text{Sm}_2\text{O}_3$ and it can be driven with a voltage below 50 volts. Also from the table it is clear that the device employing insulator having high dielectric constant has low threshold voltage. When dielectric constant of the insulating layer is low, then the threshold voltage for onset of emission is high. This can be accounted using the equivalent circuit of the device employed for explaining B-V characteristic, as shown in Fig. 5.4. We have the relation between the threshold voltage for onset of emission and applied voltage given by 5.2 as

$$U_{th} = \frac{Z_s(\omega)}{Z_i(\omega) + Z_s(\omega)} V_{th} \quad 5.3$$

The impedance offered by the insulating layer

$$Z_i = \left( R_i^2 + \frac{1}{C_i \omega^2} \right)^{1/2} \quad 5.4$$
<table>
<thead>
<tr>
<th>Insulating Material</th>
<th>Dielectric constant</th>
<th>tanδ</th>
<th>Breakdown Strength</th>
<th>$V_{th}$ of MISIM device (volts)</th>
<th>$V_{th}$ of MISIM device (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$_2$O$_3$</td>
<td>35-40</td>
<td>.02</td>
<td>$2.2 \times 10^6$V/cm</td>
<td>80</td>
<td>25</td>
</tr>
<tr>
<td>Eu$_2$O$_3$</td>
<td>15-21</td>
<td>.05</td>
<td>$2 \times 10^6$V/cm</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>Na$_3$AlF$_6$</td>
<td>6.6</td>
<td>0.40</td>
<td>$2.5 \times 10^6$V/cm</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>4.9</td>
<td>0.1</td>
<td>$2 \times 10^6$V/cm</td>
<td>120</td>
<td>65</td>
</tr>
<tr>
<td>SiO</td>
<td>3.2-5.2</td>
<td>.004-0.2</td>
<td>$2 \times 10^6$V/cm</td>
<td>125</td>
<td>70</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>4.8</td>
<td>5.5</td>
<td>$3 \times 10^6$V/cm</td>
<td>130</td>
<td>80</td>
</tr>
</tbody>
</table>
The capacitance $C_i$ is directly proportional to the dielectric constant of insulating film. Hence for devices having insulating film with high dielectric constant will have smaller $Z_i$ value, i.e., drop across the insulating layer is less. So the $U_{th}$ can be obtained at lower applied voltage. Whereas in the case of devices employing insulating films with low dielectric constant, the impedance ($Z_i$) offered by insulating film will be high and hence $U_{th}$ can be obtained only at higher applied voltages. Thus dielectric films with high dielectric constant is found to be suitable for TFEL devices for low voltage operation.

The B-V characteristic curve shows that (Figs 5.10, 11) the driving voltage for MIS structure is less than that for MISIM structure. In the latter case the effective field for acceleration of charge carriers injected from electrodes or generated in the insulating layers across ZnS layer will be greater compared with the same in device having MISIM structure. The doubly insulated TFEL device shows a remarkable increase in brightness when the applied voltage exceeds a certain value. The MIS TFEL device has no insulator layer between the electrode and ZnS layer. Thus carriers could be
readily injected from the electrode or released from the ZnS layer with the result that no carriers will accumulate near the ZnS-electrode interface, whereas in MISIM TFEL device the charges will be stored in ZnS-insulator interface. As a consequence electric field induced by space charge at ZnS insulator layer is strong and it will superpose with electric field due to the applied voltage [22]. The trapped holes inside the ZnS layer can generate an internal field which increases the probability of electrons tunneling through the ZnS-insulator barrier. Moreover, the TFEL device being a capacitive load, conduction current which contributes to luminescence is different at high voltages [22]. These factors can account for the sudden increase in brightness observed for MISIM structure devices.

The brightness of these devices were measured in absolute unit as described in Chapter-II using a PMT having spectral response closely matching that of human eye as defector. Thus the brightness of the present devices with ZnS:Mn active layer is found to be 1450 fL which is comparable with the reported values.
5.6 Aging effects of TFEL devices

It is well known that the threshold voltage for the TFEL devices increases with operating time and then gradually becomes constant [2]. Aging for more than 100 hrs. has been found to be required to stabilize the device characteristics [23]. The substrate temperature and deposition conditions are also critical for TFEL devices as they affect the maximum brightness. In the case of Y$_2$O$_3$ TFEL devices deposition of insulator layer at 473 K or annealing 723 K is found to be effective for higher brightness and it is attributed to the improvement of crystallinity of Y$_2$O$_3$ films [24].

Figures 5.12 and 5.13 shows the variation of threshold voltage with aging time for devices with Eu$_2$O$_3$ and Sm$_2$O$_3$ as insulating layers. It can be seen that devices prepared at higher substrate temperature (453 K) and subsequent annealing show little variation in the threshold voltage whereas devices prepared with cold substrate (300 K) show marked deviation in threshold voltage with operating time. It is observed that annealing can enhance the stabilization of the device more quickly. From the plot of dielectric constant and loss factors of Eu$_2$O$_3$ and Sm$_2$O$_3$ films prepared at
Fig. 5.12. Variation of threshold voltage with aging time at 1 KHz for MIS TFEL device with Eu$_2$O$_3$ as insulator.

Fig. 5.13. Variation of $V_{th}$ at 1 KHz with aging time for MIS TFEL device with Sm$_2$O$_3$ as insulator.
substrate temperature of 453 K show stable dielectric properties i.e., the variation of dielectric constant and loss factor are negligible with aging time. But in the case of these films prepared at 300 K show drastic variation in their dielectric properties with aging time. It is found that the repeated annealing of these films at 150°C enhances the stabilization of dielectric properties fairly rapidly.

The shift in B-V characteristics with time of operation (Fig. 5.14) until a final curve is achieved is considered by Inoguchi and Mito [3] to be a stabilization or aging process rather than degradation. The effect of deposition conditions on the aging behaviour of AC TFEL devices may be due to variations in the characteristics of the ZnS:Mn or insulator layers. But ZnS deposited on cold substrate (300 K) is predominantly amorphous in nature whereas films deposited at 473 K are more polycrystalline [24]. On annealing at 723°C ZnS:Mn films acquire more content with hexagonal phase.

Sasakura et al. [18] have reported that electron-beam evaporated ZnS:Mn is predominantly cubic, while Willoughly and Tuen [25] obtained a mixture of cubic and hexagonal phases in ZnS thin films prepared using
Fig. 5.14. Aging characteristic of a typical AC TFEL device with Eu₂O₃ as insulator at 1 KHz excitation frequency (T_{substrate}= 423 K).
same technique. ZnS:Mn deposited by Atomic Layer Epitaxy (ALE) method in sulphur atmosphere is purely hexagonal[26]. Hence the phase content of the ZnS film may not be critical for EL emission from manganese centers. Therefore the change in B-V characteristics and threshold voltage would depend on variations in the characteristics of the insulating layers.

Rare earth oxide films are amorphous in nature and no crystallinity was observed for films deposited at higher temperature. But the dielectric constant is found to show a constant value when prepared at higher substrate temperature. Hence the variation of the threshold voltage can be accounted using the equivalent circuits and \( U_{th} \) is given by equation 5.2. From 5.2 and 5.4 it is clear that as dielectric constant decreases with time the impedance offered by the dielectric film \( Z_i \) increases and hence voltage drops across the insulator. Thus a higher voltage is required for onset of emission. This explains why the threshold voltage for onset of emission increases with aging time. Thus the variation in threshold voltage is due to the variation in the dielectric properties of rare earth oxide films rather than in phase content of ZnS:Mn film.
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