CHAPTER VIII

FABRICATION OF THIN FILM EL DEVICES: EXPERIMENTAL SET-UP

8.1 Introduction

Thin film EL devices can be classified mainly into two categories: DC thin film and AC thin film EL devices. The former consists of an active layer of thin film phosphor in between two electrodes one of which is transparent. The other is a metal electrode. The active layer (e.g., ZnS:Cu,Mn) of these devices is prepared either by direct evaporation of the EL phosphor or by co-evaporation technique [1,2]. The devices fabricated by the co-evaporation technique are required to undergo a current forming process as discussed previously in the case of DC powder EL devices. Very high quality devices with long life have been developed (e.g., Sigmatron Nova (USA) and Sharp Corporation (Japan) though they are not freely available commercially. These devices consist of active layer ZnS:Mn in between two insulating films of high dielectric constant and of high breakdown strength. The typical structure of such a device first reported by Inoguchi et al. [3] of Sharp Corporation laboratories is shown in Fig.8.1. The materials and fabrication techniques of the various layers are as given below:

1) Transparent electrode - It is made of SnO\textsubscript{2} or In\textsubscript{2}O\textsubscript{3} using conventional thermal decomposition - oxidation method
Fig. 8.1. Typical thin film EL device structure.
(SnO₂) or vacuum evaporation method (In₂O₃) on glass substrate.

(2) Insulating layers - High dielectric strength and high dielectric constant materials like Y₂O₃, Si₃N₄, Al₂O₃ lead titanate [4], lead zirconate titanate [5] etc. also can be used. Y₂O₃ can be vacuum evaporated from an electron beam bombarded Y₂O₃ pellet; Si₃N₄ is usually reactively sputtered from Si cathode or RF sputtered from Si₃N₄ cathode in (Ar+N₂) atmosphere. Al₂O₃ is vacuum evaporated from an electron bombarded Al₂O₃ pellet or reactively sputtered from Al cathode in (Ar+O₂) atmosphere. Lead titanate and lead zirconate titanate are prepared by sputtering technique.

(3) Active layer - High purity ZnS pellet doped with Mn upto 5 wt percent is used as the source material for the deposition of EL films by means of electron bombardment. During the deposition of ZnS:Mn films, the substrate temperature is maintained around 250°C and a post deposition annealing is done around 550°C for one hour in vacuum for stabilization.

(4) Rear electrode - Usually formed by vacuum evaporated aluminium film.

(5) Protection layer - The device is protected from humidity usually with a Si₃N₄ overlayer.

The devices of the various manufacturers have essentially the same structure as described above but differ in the method of deposition of successive layers and in the technique adopted to improve the visibility under ambient
illumination. For example devices made by Sharp Corporation make use of metallic specular reflectors as the rear electrode but the ambient light reflection is eliminated by providing a circular polarizing filter at the front surface. Devices of Sigma Tron Nova make use of a black absorbing layer in between the rear dielectric layer and the back electrode which is a composite of As$_2$S$_3$ and BaTiO$_3$. Oy Lohja Corporation devices have transparent rear electrodes which make the whole device transparent. A non critical black pigment layer may also be applied to the rear surface [6]. For devices with long operating life time, different kinds of passivation layers are applied in between the successive films [7]. In view of the various requirements for the fabrication of such a device appropriate systems were built in the laboratory. They are described in this chapter.

8.2 Vacuum system for the deposition of electrodes

The metal electrodes for these devices were deposited by the vacuum evaporation technique [8,9,10]. The deposition system used was fabricated in the laboratory. It consisted of a 6" oil diffusion pump, liquid nitrogen trap and Baffle valve connected in series to a chrome plated base plate suspended on a 1m x 0.75m x 1.75m MS frame. A 550 litre/min. rotary vacuum pump was used as the backing pump. The base plate used had provision for 14 side feed throughs. A 12" glass bell jar placed over this base plate provided the vacuum chamber. Within the vacuum chamber the filament holders,
substrate holder, substrate heater, etc. were mounted on the base plate. All the high current and high voltage feed throughs needed were designed and constructed in the laboratory. The system can produce a pressure of $10^{-5}$ torr in the chamber within 45 minutes. Pressure down to $10^{-3}$ torr was measured with a Pirani gauge. The pressure below this range was monitored with a Penning gauge. A 100A transformer was used for the resistive heating of the vapour source. The various controls, gauges, high voltage and high current meters and the indicators were fitted on the front panel.

A photograph of the system is shown in Fig. 8.2. This system has provided trouble free operation for the last four years and still continues to work satisfactorily.

8.3 Deposition system for insulator and active layer films

A separate vacuum coating unit specially suited for the deposition of insulator films and the active ZnS:Mn films was fabricated. It was built using a 200 litre/minute rotary vacuum pump and a 4" oil diffusion pump. The deposition chamber consisted of a base plate covered with an SS dome with viewing windows. The diffusion pump was connected to the chamber through a liquid nitrogen trap and a baffle valve which reduced the back streaming of the oil and provided vacuum isolation between the pump and the chamber.
**Fig. 8.2.** Photograph of the vacuum coating unit fabricated for the deposition of metal films.
Conventional thermal evaporation of the doped ZnS:Mn layer was attempted as follows: An evaporation source was designed which consists of a small quartz crucible in between two molybdenum strip heaters which fully cover the crucible. By passing a high current through the strip, the crucible is uniformly heated and fairly high evaporation rate was obtained without any spattering problem. As the heater is unshielded it heats the chamber walls also and hence a metallic dome is necessary which also facilitated the deposition of the films at elevated temperatures.

**Electron beam evaporation system**

Even though the electroluminescent material of interest ZnS:Mn can be evaporated from such thermally heated evaporation sources, attempts made to evaporate good dielectric materials like Y_2O_3, Al_2O_3, SiO_2 were not successful. To achieve this, the most logical approach is to use an electron beam evaporation system specially suited for the deposition of highly pure, stoichiometric films. Moreover, materials with extremely high evaporation temperature can be easily deposited by this technique.

The simplest electron-bombardment/heating arrangement consists of a heated tungsten filament to supply electrons which are accelerated by applying a positive potential to the material for evaporation. The electrons lose their energy in the material very rapidly, their range being determined by their energy and the atomic number of the material. Thus
the surface of the material becomes molten and evaporation takes place. By the use of electron optics the beams can be focussed or can be directed onto the material for evaporation.

In the present investigation a 3 KW electron beam evaporation unit supplied by M/s. Hind High Vacuum Company is used. The schematic circuit diagram is shown in Fig.8.3.

It has a bent beam (180°) water cooled electron beam gun with 4 crucibles suitable for the deposition of four different materials, sequentially on a single substrate in one vacuum cycle. The filament heating is provided by a 10V, 30A LT transformer. The filament is kept at -6 KV, and it can be varied from -5 KV to -7 KV which facilitates a 2 mm shift in the striking point of the beam. The maximum beam current is 500 mA at 6 KV which corresponds to a maximum beam power of 3 KW. The filament voltage and the beam current can be measured on the front panel meters on the power supply unit. The evaporation rate can be controlled by adjusting the beam current. With the remote control facility this can be done by visually monitoring the source. The current and voltage stabilization in the circuit maintain the beam current and voltage irrespective of the line and load fluctuations.

8.4 Substrate heater

The active layers are usually deposited at elevated temperatures and a post deposition annealing is also required at a temperature of about 550°C. So a suitable substrate
Fig. 8.3. Schematic circuit diagram of the EBE system.
heater is needed for the fabrication of the device which can uniformly heat the substrate. A substrate heater suited for this purpose was constructed. It consists of two flat polished SS plates of 7.5 cm x 7.5 cm between which a flat kanthal wire (22 gauge) filament insulated from the metal sheet with two mica sheets is placed. The filament connections were taken through two ceramic insulation feed throughs. The glass substrates were placed on the polished surface of the heater plate and fitted firmly to it with two SS clamps. The substrate heater is positioned in the chamber such that the substrate faces the vapour source. The heater is fixed in position with ceramic insulators so that the heater support does not get heated. It is found that with a current of 3 A through the heater it can reach a temperature 550°C within 90 minutes.

8.5 Thickness measurements

8.5.1 Determination from the evaporated mass

During trials it was not necessary to measure the thickness accurately. But an idea about the thickness of the film deposited is obtained by knowing the mass evaporated from the source and applying the formula

$$t = \frac{m}{2\pi PR^2}$$

for a strip source, where

- m is the mass evaporated,
- \(P\) the density of the film,
- R the distance between the source and the substrate and
- t the thickness of the film. For filament sources the thickness
will be half of this value [11].

8.5.2. Multiple beam interferometry

Whenever the film thickness is to be measured accurately, it is done with the help of a multiple interferometric technique.

The principle of this method is based on the fact that when a partially reflecting surface is placed on a totally reflecting surface forming an air wedge and a monochromatic parallel beam of light falls on it, interference fringes are produced. The optical path difference between successive minima is \( \lambda \) which is the wavelength of the monochromatic light. If a step is formed by the thin film whose thickness is to be measured, the interference fringe pattern will be shifted as shown in Fig. 8.4. The thickness of the film can now be measured from the fringe shift \( x \) and fringe separation \( y \) as

\[
t = \frac{x}{y} \cdot \frac{\lambda}{2}
\]

This method was first used by Wiener [12] and further developed by Tolansky [13]. The experimental setup as described by Chopra [11] is used for the measurement. A travelling microscope of least count \( .001 \) mm is used to measure the fringe shift.
Fig. 8.4. The illustration of fringe shift: X is the fringe shift and Y is the fringe separation.

Quartz crystal

![Block diagram for Quartz-crystal oscillator instrumentation.](image)

Fig. 8.5. Block diagram for Quartz-crystal oscillator instrumentation.
8.5.3. Crystal film thickness monitor

A quartz-crystal thickness monitor for monitoring the rates of both deposition and evaporation of metals, non-metals and multicomponent films is the single most important monitoring device for thin film technology. Moreover it has the combined advantage of simplicity as well as high sensitivity.

The monitor utilizes the thickness shear mode of a piezo electric quartz crystal. Here the major crystal surfaces are antinodal and the mass added on either one or both sides shift the resonance frequency irrespective of the thickness, density, elastic constants or stiffness of the added material. AT cut (35°20' cut) quartz crystal is used for this purpose because of its low temperature coefficient of resonant frequency [11]. The fundamental resonance frequency for an AT cut crystal is given by

\[ f = \frac{1}{2d} \left( \frac{C}{\rho} \right)^{\frac{1}{2}} = \frac{N(\mu_{\text{H}} \text{ Hz})}{d} \]

where \( d \) is the crystal thickness, \( \rho \) its density, \( c \) its elastic constant and \( N = \left( \frac{C}{4\rho} \right)^{\frac{1}{2}} = 1670 \text{ mm H}_{\text{z}} \). The change in frequency \( \Delta f \) produced by deposited mass \( m \), added to the area \( A \) of the antinodal surface of mechanical resonator can be written as [11]

\[ \Delta f = \frac{f^2 K_m}{N \rho A} = -C_f \frac{m}{A} = -C_f t_{\text{film}} \]
where \( C = \frac{f^2K}{N\rho} \) is a constant of the crystal, and

\[ m = \Delta t \rho_{\text{film}} \]

assuming a uniform film of thickness \( t \) and a constant density \( \rho_{\text{film}} \). From the above relation it can be seen that higher sensitivity can be obtained for high frequency crystal i.e. of crystals with smaller thickness. But the relation between \( \Delta f \) and \( m \) is valid only if \( t \ll d \). So for higher frequency crystals the non linear region will be reached with smaller film thickness. As a compromise between these two factors, crystals of resonance frequency \( \sim 6 \) MHz are usually used.

The sensitivity of the crystal is limited by the variation in crystal frequency due to changes in temperature, oscillator drive level etc. The latter is more severe since the crystals are to be mounted in the deposition chamber so as to see the evaporation source. So they are mounted in water cooled electrically shielded crystal holders. In order to eliminate the possible damage to the control circuit due to electrostatic pick up especially when used with EBB system the crystal electrode facing the source is grounded.

The frequency changes in the quartz crystal oscillator can be directly measured with a frequency counter having an accuracy of 1 Hz in the MHz range. But with a heterodyning technique a less expensive meter readout for this small frequency shift can be obtained. In this method, by beating the frequency of the monitor crystal with that of another quartz crystal of a slightly different frequency a beat
frequency is obtained. This is then mixed with the output from another variable frequency oscillator and a second intermediate frequency is obtained. It is then amplified, rectified and read on a meter. The rate of change of frequency can be obtained by an RC differentiating circuit. The block diagram of such a circuit is shown in Fig. 8.5.

In the present case the thickness of the various layers deposited for the fabrication of the device was monitored with a (Hind High vacuum, model CFM-l) quartz film thickness monitor. In this system a 6 MHz monitor crystal is mounted on a water cooled crystal holder and placed inside the vacuum chamber. The reference crystal is of 6.5 MHz and is kept inside the control unit. Here the difference between the crystal frequencies is amplified and fed into another circuit where it is mixed with a variable oscillator so as to produce a final difference frequency between 0 and 100 KHz. As discussed above, the mass of the deposited material causes a reduction in the natural resonant frequency of the monitor crystal, causing an increase in the final difference frequency. This change is converted into a DC signal which actuates both the frequency shift meter and the rate change meter. The frequency shift meter reading can be reset to zero by changing the frequency of the variable oscillator and it can be done with an external reset control.

The meter readout in the thickness monitor provides the film thickness in terms of the frequency shift. So it
has to be translated into thickness value in absolute units using proper calibration procedure. For this the crystal monitor head is fixed in the deposition chamber such that it can see the vapour source and is kept at a distance equal to that of the substrate from the source. A weighed amount of MgF₂ is taken in a molybdenum boat and evaporated at a pressure of 10⁻⁵ torr, noting the frequency shift in the thickness monitor. The substrate was taken out and the thickness was measured with Fizeau fringe method described in Section 8.5.2. From this the film thickness in terms of the change in frequency is found out, which will remain the same as the relative position of the thickness monitor, substrate and the source are not changed. For example if a frequency shift of 1000 Hz is noted for a film thickness of 200 nm, then 2 nm thickness corresponds to frequency shift of 10 Hz for MgF₂ film. For other materials thickness can be found by knowing the frequency shift and their densities. If the relative position of the substrate, the crystal or the source is changed the system is recalibrated for the new configuration. With this system in conjunction with the EBE system, films of Y₂O₃, ZnS:Mn, SiO₂, Nb₂O₅, MgF₂, etc. have been successfully deposited to required thickness values. Fig.8.6 shows the whole experimental setup used for the fabrication of the device.

8.6. Deposition of transparent conducting electrode of SnO₂ by Spray Pyrolysis method

Non stoichiometric and doped films of oxides of tin, indium, cadmium, zinc and their various alloys, deposited by
Fig. 8.6. Photograph of the setup used for the fabrication of TFEL cells
numerous techniques exhibit high transmittance in the visible region, high reflectance in the IR and nearly metallic conductivity. The electrical as well as the optical properties of these unusual materials can be tailored by controlling the deposition parameters. Among them the most prominent one is that of oxides of Indium and tin doped with appropriate dopants. These transparent coatings find application as transparent electrodes in various electro-optic devices, as resistors, transparent heating elements for aircraft and automobile windows, antistatic coatings for instrument windows, heat reflecting mirrors for glass windows and in incandescent bulbs; anti-reflection coatings, selective absorber interconnections in solar heat collectors, gas sensors, touch sensitive switches etc. [14].

Because of their immense technological importance, extensive investigation is being carried out especially in the preparation and characterisation of these films. It is found that the quality of the film obtained depends largely on the method adopted for the preparation. By almost all thin film deposition techniques such films have been prepared. They include the post deposition oxidation of metal[15], reactive evaporation [16], direct evaporation by thermal [17] and EBE [18], sputtering [19], reactive ion plating [20], chemical vapour deposition [21], spray pyrolysis [22], Dip technique [23], chemical solution growth [1] etc. The film of best quality was that of indium doped tin oxide obtained by spray pyrolysis. Next is the sputtered film of ITO [1].
As the transparent electrode for the present EL devices tin oxide film obtained by spray pyrolysis method was used. This method was selected because it can yield high quality film with a comparatively simple experimental setup.

In the present case, an aqueous SnCl$_4$.5H$_2$O solution taken with excess amount of isopropyl alcohol was sprayed on to a heated glass substrate. The spray strikes the substrates at an oblique angle and the entire process is done in a good stream of air or oxygen. The details of the setup in the present case are described below.

The glass substrate to be coated was first cleaned in soap solution and in chromic acid. It was then placed on a hot plate made of stainless steel which could be heated upto 500$^\circ$C. A good stream of air was made to flow from an electric fan. The spray solution was taken in a special chromatographic sprayer. The spray was produced by blowing compressed air into the sprayer and was controlled by adjusting the air pressure. Spraying was done such that it hits the hot substrate at about 45$^\circ$. The air stream and the spray from the nozzle of the sprayer carried away the residual gases which mainly consisted of HCl and alcohol vapour.

A number of trials were made with different concentrations of spray solution and with different substrate temperatures. In the present case a saturated solution of SnCl$_4$.5H$_2$O at room temperature in isopropyl alcohol sprayed on a glass plate
kept at 400°C gave the best films with a sheet resistance of 80 Ω/sq. and transmittance ~85 percent.

Selective removal of the SnO₂ films was done by reacting it with nascent hydrogen. The films prepared has good adhesinn to the substrate, and it could be subjected to ordinary cleaning methods which facilitated its repeated use. But a prolonged acid treatment was found to destroy the film.

8.7. Summary

An outline of a typical AC thin film EL device is given together with an account of the deposition techniques for the various films used in them. Different experimental setup developed in the laboratory to fabricate such a device is explained. The method of deposition of transparent conducting electrode of SnO₂ is described at the end of the chapter.

References


7. P.N.R. Panicker; Sigmatron Nova (Private Communication)


