Research Article

HIGH EFFICIENT ZnS:Mn THIN- FILM ELECTROLUMINESCENT DEVICES

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ABSTRACT
We have planned to make the investigation of ZnS:Mn thin film electroluminescent devices with MgF₂ dielectric layers. In the pasty most of the studies on thin film EL have been made on the ZnS:Mn, which emits in the yellow region. The insulating material MgF₂ has been chosen because its dielectric breakdown voltage is very high (2 x 10⁶ V/cm) as well as its dielectric constant is also very high (ε₂ = 4.9). It is to be noted that the dielectric loss factor of MgF₂ depends strongly on the frequency of the excitation field. Moreover, thin film of MgF₂ can be made easily by thermal evaporation as well as by electron beam evaporation techniques. Electroluminescent device structures consisting of metal/dielectric/ZnS:Mn /dielectric. The Electroluminescent devices were operated under alternating current bias (175 peak voltage).

Key Words: Electroluminescence, Activators, Active Layer, Electroluminescent Centre, Vacuum Coating Unit

INTRODUCTION
The thin film EL device consists of an active layer of thin film phosphor in between two electrodes, one of which is transparent and the other is a metal electrode. The active layer (e.g. ZnS:Mn) of these devices is prepared either by direct evaporation of the EL phosphor or by co-evaporation technique. ZnS:Mn is by far the most stable and efficient material in both Electroluminescence (EL) and Photoluminescence (PL). ZnS can crystallize in both Blende and Wurtzite structures, depending on the preparation conditions and on the amount of Mn. the forbidden gap, Eg of the two structures differ only slightly. For the Blende structure Eg ≈ 3.7eV, and for the hexagonal E ≈ 3.7eV, both at T = 4.2K. The luminescence emission owing to Mn is assigned to the internal transition ¹T₁(G) → ⁶H₁(S) of Mn⁻² in tetrahedral coordination of neighboring sulfur ions.

Emission occurs at a somewhat lower energy than the first excited level (¹T₁) above the ground state (2.24 eV) owing to Stokes shifts. Since the transition is spin and parity-forbidden, the lifetime τ₀ of the isolated ion is rather long: 1.15 to 1.17 ms, depending on the ZnS crystalline structure (hexagonal, cubic) for PL (Gumlich, 1981). The observed decay times of TFEL correspond to these data. One finds 1.3 ms for thin films that have been grown by ALE (Benoit et al., 1988). ALE films seen to have a predominantly hexagonal structure (Busse et al., 1983). Films grown by electron-beam evaporation, which are expected to have cubic structure, lead to 1.7 ms (Benoit et al., 1988). When the Mn concentration exceeds about 0.1 mo 1%, the decay curve becomes non exponential with a decay time τ< spp — owing to energy diffusion between Mn centres. This process favours non radiative de-excitation, and as consequence the radiative efficiency η_rad (ratio of the emitting centres to excited ones) decreases compared to η_rad for the isolated ion. When the critical density of excited Mn centres is reached (at high drive level), interaction between excited becomes relevant, resulting efficiency (Benoit et al., 1988).

Very recently the Mn transition 3d⁵ → 3d⁴ 4p¹ has also been detected by using Fano resonances. Mertins (1995) excited the Mn ⁴T₁(G) → ⁶H₁(S) emission by synchrotron radiation. Obviously the
empty $\text{Mn}^4p$ States are degenerate with the continuum of the ZnS conduction band, which allows the excitation in Fano resonances. The energy of the transitions $3d^5 \rightarrow 3d^44p^1$ is tentatively determined to lie within the range 5-10 eV.

**MATERIALS AND METHODS**

We have prepared ZnS:Mn phosphors by following the method described below:

**Base Material**

The luminescent grade ZnS can be prepared easily in laboratory following the procedure given in the literature (Leverenz 1950). However, now a day several chemical companies are supplying luminescent grade ZnS which save a lot of effort in the phosphor preparation. For our investigation we have used luminescent grade ZnS supplied by the chemical companies.

**Flux**

NaCl has been found to be suitable flux for preparing ZnS phosphors. The amount of flux can be from 2 to 20 percent, but in the present investigation the flux has been taken as 3 per cent of the matrix.

**Activator**

The luminescent properties of ZnS phosphors are frequently due to the presence of small amount of cations impurities. The element which play the role of activators are usually of the transition metals or post-transition metals such as copper, manganese, silver, gold, chromium, lead, bismuth and samarium, or the rare earths such as terbium, thallium, samarium, europium, etc.

![Apparatus used for preparing conducting glass plate](image)

**Figure 1: Apparatus used for preparing conducting glass plate**

Mn was used as activators in the present investigation. For doping Mn, measured amount of MnCl$_2$ (A.R. Grade) was dissolved in the nitric acid and then diluted with distilled water to make the required standard solution. For the present investigations, the activator concentration in phosphors was varied from 0 to 10,000 ppm.

**Preparation of charges**

Mn (0.5 wt %) doped ZnS powder was prepared from finely ground mixtures of highly pure (99.999%) ZnS powder and a trace of MnCl$_2$ with required amount of flux. The doping concentration was kept at 0.5 wt% to avoid line broadening due to dipole-dipole interaction as well as to obtain maximum
luminance of EL Device. The mixtures were placed in alumina crucible and fired for 1 hour at a temperature about $1000^\circ$C under $N_2$ atmosphere. The fired powder was pressed into the pellets to deposit ZnS:Mn thin films.

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Method of firing
The charge prepared following the method described previously was transferred into a clean silica boat. Another similar empty boat was placed over this. The two boats stick together, forming an air tight enclosure to the charge. Then these boats were placed in the central part of the muffle furnace shown in
Fig 3. The time of firing was two hours and temperatures were 900°C (cubic) and 1100° (hexagonal). After two hours the charge was taken out and pulverized. This ensures the effective trapping of activator atoms, as a result of very rapid cooling. The phosphors were washed with distilled water three or four times. The phosphor was then dried and stored in a clean, dry container and sealed with wax to avoid any contact with moisture. The ZnS:Mn (cubic) phosphors were prepared at 900°C.

Table 1 shows the details of the phosphor preparation.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Ingredients</th>
<th>Simplified Notation of Phosphors</th>
<th>Firing Temperature</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 gms ZnS+0.000000 gmMnCl₂ + 0.1 NaCl</td>
<td>ZnS : Mn</td>
<td>900°C</td>
<td>000 ppm</td>
</tr>
<tr>
<td>2</td>
<td>5 gms ZnS+0.000000 gmMnCl₂ + 0.1 NaCl</td>
<td>ZnS : Mn</td>
<td>900°C</td>
<td>100 ppm</td>
</tr>
<tr>
<td>3</td>
<td>5 gms ZnS+0.005367 gmMnCl₂ + 0.1 NaCl</td>
<td>ZnS : Mn</td>
<td>900°C</td>
<td>300 ppm</td>
</tr>
<tr>
<td>4</td>
<td>5 gms ZnS+0.008945 gmMnCl₂ + 0.1 NaCl</td>
<td>ZnS : Mn</td>
<td>900°C</td>
<td>500 ppm</td>
</tr>
<tr>
<td>5</td>
<td>5 gms ZnS+0.178906 gmMnCl₂ + 0.1 NaCl</td>
<td>ZnS : Mn</td>
<td>900°C</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>6</td>
<td>5 gms ZnS+0.005367 gmMnCl₂ + 0.1 NaCl</td>
<td>ZnS : Mn</td>
<td>900°C</td>
<td>3000 ppm</td>
</tr>
<tr>
<td>7</td>
<td>5 gms ZnS+0.08945 gmMnCl₂ + 0.1 NaCl</td>
<td>ZnS : Mn</td>
<td>900°C</td>
<td>5000 ppm</td>
</tr>
<tr>
<td>8</td>
<td>5 gms ZnS+0.0178906 gmMnCl₂ + 0.1 NaCl</td>
<td>ZnS : Mn</td>
<td>900°C</td>
<td>1000 ppm</td>
</tr>
</tbody>
</table>

It was found that the EL brightness of cubic phosphors is several times higher as compared to hexagonal phosphors. Therefore, in the present investigation the cubic phosphors of ZnS:Mn, was only used for the preparation of the active layer of the electroluminescent device.

**Deposition of transparent conducting electrode of SnO₂**

Non-stoichiometric and doped films of oxides of tin, indium, cadmium, zinc and their various alloys, deposited by numerous technique exhibit high transmittance in the visible region, highly 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 coating find application as transparent electrodes in various electro-optic devices, as resistors, transparent heating elements for instrument windows, heat reflecting mirrors for glass windows and in incandescent bulbs; anti-reflection coating, selective absorber interconnections in solar heat collectors, gas sensors, touch sensitive switches, etc (Chopra et al., 1983).

Because of their immense technological importance, extensive investigation is being carried out especially in the preparation and characterization of these films. It is found that the quality of the film obtained depends largely on the method adopter for the preparation. BY almost all thin film deposition techniques, such films have been prepared. They include the post deposition oxidation of metal (Nishino and Hamakawa, 1970).
To obtain conducting electrodes, different workers have used different methods. In the present investigation, we have used the method suggested by Gomer (1953) with a little improvement. The conducting glass plate used for purpose is ordinary micro slides of 2.5 cm x 7.5 cm size. The glass plates were heated slowly up to 500°C by placing them over a thick metallic plate and the vapours of SnCl₂ were sprayed over the heated glass plate in the presence of air. The device consists of a flask in which the crystals of SnCl₂ were placed and heated to vapourise the SnCl₂. The vapours were blown towards the glass plate by an air blower. The vapours of SnCl₂ mixed with air were deposited on the surface of heated glass plate SnO₂. This process was repeated until the desired results were obtained. The shoot resistance of conducting glass plates was nearly 50 ohm cm⁻².

**Deposition system for insulator, active layer and electrode**

The thin film of insulator MgF₂, active layer ZnS:Mn, and metal electrode (Al) were deposited by using a thin film vacuum coating unit supplied by M/S Hind High Vacuum Company. The coating unit contains a rotary vacuum pump and an oil diffusion pump. The deposition chamber consists of a base plate with viewing windows. The diffusion pump was connected to the chamber through a liquid nitrogen trap and a baffle valve reduced the back streaming of the oil and provided vacuum isolation between the pump and chamber.

An evaporation source consists of a small molybdenum boat. The crucible in uniformly heated and fairly evaporation rate was obtained without any sputtering problem. The thin films of ZnS:Mn, were deposited at 250°C by heating the substrate. After the deposition of second layer of MgF₂ the device so formed is taken out of the coating unit. Then a mica mask is placed over the MgF₂ film and this structure is placed inside the coating unit and the vacuum of the order of 2 x 10⁻⁵ torr was produced and the Al film was deposited through a mica mask suitably prepared so that on each substrate-aluminium electrode strips of 2 cm x 0.3 cm were formed. This produced seven identical cells each of emitting area 0.4 cm². Then the EL derive this formed is annealed at 550°C for one hour.

As the unbaked MgF₂ is highly sensitive to moisture, adequate measure was taken to reduce the humidity in the laboratory and immediately on removal from the chamber the device was transferred to a desiccators. While is use, these devices were covered with a glass plate and the sides were sealed with cellophane tape. Such protected devices could be operated for weeks without any deterioration.

The thin films of MgF₂ and Al were deposited at room temperature. Generally, the thickness of the thin films deposited were as given below: MgF₂ - 3000Å, ZnS:Mn - 6000 Å, MgF₂ - 3000Å, and Al - 4000 Å. In some cases the films of different thickness were also deposited.

**DISCUSSION**

The device of the various manufactures 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. In summary, we demonstrated ac-driven electroluminescence from highly efficient and stable ZnS:Mn. Our device structures contain standard wide band gap materials which eliminate charge injection into the devices. Because the demonstrate device architecture is comparable to existing ACTFEL technology, our use of vacuum coating to deposit the multilayer stacks highlights the viability of solution-based techniques of depositing the active phosphor layer in ACTFEL devices, which could enable print fabrication of transparent multicolor ACTFEL displays.

**REFERENCES**


