CHAPTER SEVEN

Low temperature fabrication of SrS:Cu,F ACTFEL device by electron beam evaporation

7.1 Abstract

The deposition of highly stoichiometric SrS:Cu,F films and fabrication of a multilayer ACTFEL device based on it is presented. The device exhibited bluish white EL emission with chromaticity coordinates $x = 0.25$, $y = 0.27$ and low threshold voltage.

7.2 Introduction

To replicate full colour performance of a cathode ray tube, efficient EL active red, green and blue phosphors having specific emission colour must be available. The prospects for production of a full-colour EL display have brightened considerably following the discovery and efficient operation of the blue emitting phosphor SrS:Cu and its modifications [1]. For SrS based EL devices the phosphor layer is deposited at substrate temperatures 400°C-600°C and sulphur co evaporation to realize stoichiometric films [2,3]. For the films deposited at low temperatures post deposition annealing should be performed at high temperatures in the range 650°C-850°C [4-8].

We report a new method of deposition of SrS:Cu,F films at a substrate temperature 380°C without sulphur co evaporation and post deposition annealing. This was carried out via EB/thermal multi-source evaporation.
7.3 Experimental

Strontium sulphide pellets for evaporation were prepared by pressing the mixed powder of SrS, polyvinyl alcohol (PVA) and 5wt. % of NH₄Cl, by applying a pressure of 4 tonnes. This pellet was sintered at a ramp rate of 3°C/minute to 850°C and then holding the temperature at 850°C for two hours. The source material for activator was 99.9% pure CuF₂ which was evaporated from an alumina crucible heated with a tungsten wire heater. The sintered SrS pellets were electron beam evaporated while CuF₂ was thermally evaporated yielding SrS:Cu₃F film. Before opening the shutter the chamber was purged with thermally evaporated sulphur from the crucible containing the activator.

Figure 7.1 shows the structure of EL device fabricated. The substrate used was glass coated with indium tin oxide (ITO) and aluminium titanium oxide (ATO) supplied by Planar. The Zinc sulphide buffer layers each of thickness ~150 nm were deposited by EB evaporation at a substrate temperature of 150°C. The Y₂O₃ top insulating layer was also grown by EB evaporation at 200°C with a thickness ~200 nm. The thickness of the phosphor layer was ~700 nm. The chamber vacuum prior to evaporation was 5×10⁻⁶ mbar and the temperature of the glass substrate was 380°C. The crystallinity of the films were analysed by x-ray diffraction (XRD) using a Rigaku x-ray diffractometer with Cu Kα x-ray. The PL and PLE spectra were recorded with Jobin Yvon Fluoromax-3 Flourimeter. The optical band gap of pure SrS was estimated from the transmission spectra recorded with Jasco-V-570 uv-vis-nir spectrophotometer. The surface roughness of the samples were estimated by atomic force microscopy (AFM). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed to determine the
chemical composition of pure SrS powder. A 0.32 m monochromator (Triax-320) coupled with Hamamatsu R928 photomultiplier tube was used to record the electroluminescent output from the fabricated device. Thickness of the samples were measured by using stylus thickness profiler.

![Diagram of SrS:Cu,F multilayer ACTFEL device](image)

**Figure 7.1:** Structure of the SrS:Cu,F multilayer ACTFEL device

### 7.4 Results and discussion

X-ray diffraction patterns of SrS:Cu,F thin film and the device are shown in figure 7.2. Polycrystalline film of SrS:Cu,F with reflections matching with JCPDS file no.8-489 for cubic SrS was obtained. In the x-ray diffraction pattern of the device only reflections from ITO and SrS were observed. No reflection was observed for ZnS possibly because it may be too thin and intensity may be weak. To confirm this a 600nm thick film of ZnS was electron beam evaporated on a glass substrate at 150°C. The x-ray diffraction pattern of this film shows the growth of ZnS in cubic phase (figure 7.3).
Similarly a 500nm thick film of Y$_2$O$_3$ was electron beam evaporated on glass substrate at 200°C and it was found to be amorphous from XRD analysis. No diffraction peaks were observed for ATO also as in the substrate since this layer was amorphous.

Because of the high field nature of the thin film EL device, it is desirable to have a smooth interface between the various film layers. Any asperity will lead to a high field region that may lead to localized breakdown of the device structure. Therefore it is preferable to have either a fine grained insulating layer morphology or even better an amorphous structure. The amorphous structure leads to better device stability by eliminating possible grain boundary diffusion paths for ions or moisture.

Figure 7.4 is the typical AFM images of SrS:Cu,F thin film with a thickness of 700nm. Large grain size is necessary to permit the electric field to accelerate electrons to high energies before they are scattered at grain boundaries [9]. From the AFM images the samples were observed to contain a continuous network of flat areas with a root mean square (rms) surface roughness < 10nm, having heights exceeding 100nm in many places.
Figure 7.2 (a). Plot of JCPDS data of pure SrS and x-ray diffraction patterns of (b). SrS:Cu,F thin film, (c). glass/ITO/ATO substrate and (d). SrS:Cu,F multilayer device.

Figure 7.3. X-ray diffraction pattern of ZnS film on glass substrate deposited at 150°C
To evaluate the band gap of SrS, pure SrS was coated on a glass substrate at a substrate temperature 380°C after purging the chamber with sulphur. Crystalline growth was confirmed by XRD. Figure 7.5 shows the transmission of undoped SrS thin film which exhibited a transmission >85% in the visible region. The absorption coefficient $\alpha$ was evaluated using the measured value of thickness $'t'$ using the relation $I = I_0 e^{-\alpha t}$. The optical absorption coefficient $'\alpha'$ near the absorption edge is given by $\alpha \approx A (h\nu - E_{\text{op}})^{1/2} / h\nu$. The direct band gap of SrS thin film was estimated by plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$ and extrapolating the linear portion near the onset of
absorption edge to the energy axis. A typical $(\alpha h\nu)^2$ vs. $h\nu$ plot of SrS film is shown in the inset of figure 7.5.

![Transmission spectrum of undoped SrS](image)

**Figure 7.5.** Transmission spectrum of undoped SrS. Inset shows the $(\alpha h\nu)^2$ vs. $h\nu$ plot of SrS film.

SrS:Cu,F thin film was deposited on glass substrate at 380°C by electron beam evaporation after purging the chamber with sulphur. X ray diffraction (figure 7.2) and photoluminescence measurements of the film were (figure 7.6) recorded. The PL spectrum of SrS:Cu,F thin film had two bands: one main band centered at 535nm and another weak but broad band peaked at 435nm. The emission at 535nm is due to the $3d^94s^1(3^2E_g)\rightarrow3d^{10}(^1A_{1g})$ [10] transition of the Cu+ isolated ions in octahedral symmetry environment. The $3d^{10}\rightarrow3d^94s^1$ electronic transitions are parity- and J-forbidden in the free Cu+ ion. In SrS lattice, the selection rules forbidding the transitions are relaxed.
by several factors. The first factor is electron-lattice interactions which make this transition partially allowed. The second factor is the off-center position of Cu+ ions which relaxes the forbidding selecton rules of the inversion symmetry by lowering the symmetry of Cu+ centers. The off-center position of Cu+ ions refers to the shift of Cu+ ions substituting for Sr in SrS lattice from the exact Sr position. This is possible because ionic radius of Cu+ ions (0.77Å) [10] is significantly smaller than Sr2+ ions (1.18Å) and has space available to be loosely bound on the cation site. The broad emission band at 435nm can be ascribed to donor acceptor recombination.

The photoluminescence excitation spectrum of SrS:Cu,F thin film monitored at an emission wavelength 535nm, contained a broad band peaked at 320nm which is ascribed to \( {^1}A_{1g} \rightarrow {^1}E_g \) transition in Cu+ centers.

Figure 7.6. The photoluminescence spectrum of SrS:Cu,F thin film deposited at 380°C on glass substrate
The photoluminescence and electroluminescence spectra of SrS,Cu ACTFEL device are shown in figure 7.7. PL emission from the device structure under excitation with 320nm consisted of two main peaks, one at 380 nm and other at 434 nm. The less intense broad emission at 435nm observed in SrS:Cu,F thin film appeared as two resolved peaks in the device at 380nm and 435nm. Li et al. reported a PL emission peak at 440 nm for SrS:Cu film which was assigned to donor acceptor recombination [11]. The peak at 380nm was also present in the host SrS which is thought to be due to sulphur vacancies (Fig.7.8). From the AES analysis sulphur to strontium ratio of the SrS powder was found to be 0.78.

![Photoluminescence and electroluminescence spectra of SrS:Cu,F multilayer device](image-url)
Electroluminescence spectrum consisted of an additional broad emission centered at 535nm. This arises due to aggregated copper pairs or \([\text{Cu}^+_{\text{Sr}}]^-\) centers with coordination number 5 \([12,13]\).

![Figure 7.8. PLE and PL spectra of pure SrS at room temperature.](image)

The luminescence mechanism in the device can be explained using the model shown in figure 7.9. Cu enters the SrS lattice as an acceptor that is single negatively charged in equilibrium.

Sulphur vacancies which are double donors are formed at 1.09eV below the conduction band. Excitation in the device takes place via \(^1\text{A}_\text{lg} \rightarrow ^1\text{E}_\text{g}\) transition in Cu+ centers. The low energy emission band at 535nm is due to transition...
in Cu\textsuperscript{+} levels whereas the other two emission bands (380nm and 435nm) are from the sulphur vacancies to [Cu\textsubscript{Sr}]\textsuperscript{−} and valence band. It has been suggested that a recombination process similar to the well known ZnS:Cu mechanism could also be valid for the copper doped alkaline earth sulphides\cite{14,15}. All the layers were coated in vacuum. This might have aided the formation of more sulphur vacancies in the film thereby enhancing the intensity of high energy bands in the device than in the SrS:Cu,F thin film.

The device gave a blue PL emission with CIE coordinates \(x=0.18\) and \(y=0.17\) at an excitation wavelength of 320nm whereas the EL emission was bluish white with CIE coordinates \(x=0.25\) and \(y=0.27\) [Fig.7.10]. This is due

Figure 7.9. Schematic energy levels of (a) Cu doped SrS and (b) Cu\textsuperscript{+} ion in the crystal field with octahedral symmetry.
to the additional broad emission centered at 535 nm in the EL spectrum. There are reports of whitish blue EL emission from SrS:Cu thin film electroluminescent devices [16].

Figure 7.10. CIE chromaticity diagram showing the colour coordinates of PL and EL in SrS:Cu,F multilayer device.

To observe electroluminescence the device was driven by a bipolar trapezoidal voltage of 1.2 kHz. The brightness- voltage characteristics of the device is shown in figure 7.11.
7.5 Conclusion

We have demonstrated that high quality SrS:Cu,F films can be conveniently deposited on glass substrate without post-annealing and sulphur coevaporation. A device with ZnS buffer layer was fabricated by this method. PL emission of the device was blue whereas EL emission yellowish white in colour. This is due to the presence of an additional emission band at 535nm in EL spectrum. A possible model for the emission mechanism in the device is suggested.
7.6 References
