THE ROLE OF GALLIUM SULFIDE IN SrS:Ce GRAIN GROWTH

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Whereas efficient red (ZnS:Mn) and green (ZnS:Tb) phosphors are available for full-color flat-panel display technology, efficient blue phosphors are still under development. SrS:Ce is being investigated as a suitable material. As part of a larger study, annealed SrS:Ce films produced from sputter targets incorporating Ga₂S₃ were found to be five times brighter than films produced from targets containing no Ga₂S₃. Consequently, the significance of added gallium sulfide to the morphology of SrS:Ce films during annealing is being investigated.

Following deposition, plan view specimens of films were prepared for transmission electron microscopy by mechanical grinding, dimpling, and Ar⁺ milling. Films were examined in a Philips CM12, and a JEOL 200CX. Additionally, EDS line scans were obtained in the scanning-transmission mode of a Philips CM200FEG, integrated with an EMiSPEC Vision acquisition system. The EDS line scans were defined as a series of 40 points along a line, spaced approximately 3.6 nm apart. The dwell time for EDS acquisition at each point was 10 sec.

As-deposited films produced with no Ga₂S₃ are columnar in cross-section, but appear equiaxed in the plane of the film. Typical grain diameters are 10-75 nm (Fig. 1). Upon annealing at 810°C for 120 s, the grains have coarsened to be 55-90 nm in diameter (Fig. 2). As-deposited films produced with Ga₂S₃ incorporated in the sputter target (Fig. 3a) have a morphology in the plane of the film similar to that of Fig. 1. Diffraction patterns (Fig. 3b) from this film indicate that equilibrium cubic SrS phase is the only crystalline phase present. Energy dispersive X-ray spectrometry (EDS) across regions approximately 2.5 μm in diameter indicated the film contained approximately 1 at. % Ce and 2 at. % Ga.

Annealing the Ga₂S₃-containing film at 810°C for 120 s resulted in significant grain growth; the matrix consists of typically 250-600 nm-diameter grains (Fig. 4a). The diffraction pattern from grain 'd' in Fig 4a is shown in Fig. 4b and confirms this large grain is SrS (indexes as b=[001]). The EDS analysis indicates that the smaller intra- and intergranular precipitates, marked 'e' in Fig. 4a, are Ce-enriched relative to the SrS grains. Additionally, material within some grain boundary triple points ('f' in Fig. 4a) was found to be amorphous (Fig. 4c). An annular dark-field STEM image (Fig. 5) shows the position of the EDS line profile (from 'a' to 'a'') acquired across a grain boundary triple point (Fig. 5) which contained amorphous material. The resulting profiles are shown as Fig. 6. Relative to the adjacent SrS grain, the amorphous phase is significantly enriched in Ga. Intensities from points in the region of maximum Ga (~40 - 62 nm) were summed, as were intensities from points within the SrS grain, far from the amorphous phase (~128 - 142 nm). These indicated the amorphous phase contained 44 at. % Ga, and the SrS grain <1 at. % Ga. Additionally, a Ce-rich precipitate, not readily discerned in the image, was also revealed by the EDS line profile.

The addition of Ga₂S₃ increases the brightness of SrS:Ce films by enhancing grain growth during annealing. Also being investigated is the possibility that Ga₂S₃, either as a sub-sulfide or as a source of Ga, is involved in a liquid-phase sintering mechanism, which would account for the increased grain growth observed after annealing.¹

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FIG. 1 - As-deposited SrS:Ce sputtered film.

FIG. 2 - SrS:Ce sputtered film, annealed at 810°C for 120 s.

FIG. 3 - a) Ga_2S_3 -incorporated, as-deposited SrS:Ce film; and b) diffraction pattern.

FIG. 4 - a) Ga_2S_3 -incorporated, SrS:Ce film, annealed at 810°C for 120 s; diffraction patterns from b) SrS and c) amorphous phase.

FIG. 5 - Amorphous grain boundary triple point used for EDS line scan (from a to a').

FIG. 6 - EDS profiles across aa'

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