

# Oxidation and diffusion of Cu in SrS: Cu grown by MBE for blue phosphors

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## Abstract

Systematic studies of MBE grown SrS:Cu thin film blue phosphors are reported. It was found that Cu was not oxidized in the as-grown SrS:Cu films. The oxidation and diffusion of Cu during the postgrowth annealing in a H<sub>2</sub>S atmosphere were identified as the key reasons for the dramatically improved grain size and luminescent properties reported earlier. Experimental evidence of the oxidation states of Cu and the diffusion dynamics of Cu ions in SrS:Cu and SrS:Cu,Mn films will be presented and discussed. © 2000 Published by Elsevier Science B.V.

*Keywords:* SrS:Cu; Oxidation; Diffusion

## 1. Introduction

Thin film SrS:Cu is a potential candidate for blue electro-luminescent (EL) phosphors. Although recent developments have greatly increased the luminescent efficiency at wavelengths in the blue range [1], the efficiency of the best SrS:Cu EL device is still only half of the value required for a high brightness VGA display. Currently, the most efficient SrS:Cu blue EL phosphors are prepared by magnetron sputtering deposition followed by a postgrowth annealing at 810°C. However, this process precludes the applicability of low temperature glass substrates. Therefore, developing a low temperature process technique is vitally important for low price applications in high brightness large area displays.

In molecular beam epitaxially deposited SrS:Cu films, it was found that the luminescence from as-grown SrS:Cu films was very weak. In a previous publication, we showed that postgrowth annealing in a H<sub>2</sub>S atmosphere dramatically increased the grain size and improved the luminescent properties [2]. From considerations of the electro-negativity of Cu and the much larger free energy of formation for Cu<sub>2</sub>S than that for SrS, it was proposed that Cu remained as atomic Cu instead of becoming a substitutional Cu<sup>+</sup> ion during the growth of the SrS film. During annealing at relatively high temperature in a H<sub>2</sub>S atmosphere, it is proposed

that the Cu atoms are ionized into Cu<sup>+</sup> ions and diffuse into the SrS lattice. The weak luminescence in the as-grown films was attributed to the segregation of Cu atoms at the grain boundaries. The ionization of atomic Cu by H<sub>2</sub>S and the diffusion of Cu<sup>+</sup> into the SrS lattice during annealing were believed to be responsible for the grain growth and the improved luminescent property [2].

Evidence for the valence states of Cu and the diffusion of Cu<sup>+</sup> ions into the SrS lattice has been obtained experimentally. In a study on the reaction of Cu with H<sub>2</sub>S, the oxidation states of copper in the as-grown and annealed samples were verified. By introducing Mn into SrS:Cu, a Mn related second phase was identified on the grain boundary. By investigating the competing effects of Cu and Mn on the grain growth in the SrS:Cu,Mn system, a deeper understanding has been obtained on the oxidization and diffusion mechanisms of Cu in SrS films.

## 2. Experimental procedure

SrS:Cu thin films were grown on ATO/ITO/glass substrates provided by Planar America. Growth was performed in a MBE system. Pyrolytic boron nitride (pBN) crucibles were used for the evaporation of solid host and dopant materials. A H<sub>2</sub>S gas source was used as a sulfur precursor and delivered through a MKS 1159 mass flow controller. In this study, the strontium flux was  $F_{\text{Sr}} = 7.5 \times 10^{-7}$  Torr, Cu fluxes were in the range of  $5 \times 10^{-9}$ – $2.0 \times 10^{-8}$  Torr, the H<sub>2</sub>S flow rates were

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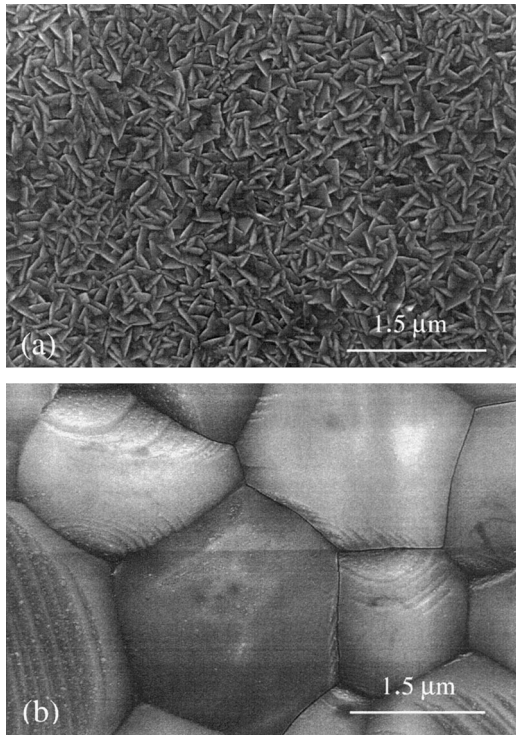


Fig. 1. Morphology of as-grown and annealed SrS:Cu films: (a) as-grown; (b) annealed at 750°C for 1 min followed by 650°C for 20 min with H<sub>2</sub>S flow rate of 3.2 sccm.

4.5–8.0 sccm, and the growth temperatures were 400–600°C. The growth rates were 0.4–1.0 μm/h and the film thickness was 1.0 μm. Postgrowth annealing was performed in the MBE chamber with a H<sub>2</sub>S flux. The annealing temperatures were between 600 and 750°C for periods up to 15 min. During annealing the H<sub>2</sub>S flow rate was 3.2 sccm.

X-ray diffraction (XRD), scanning electron microscopy

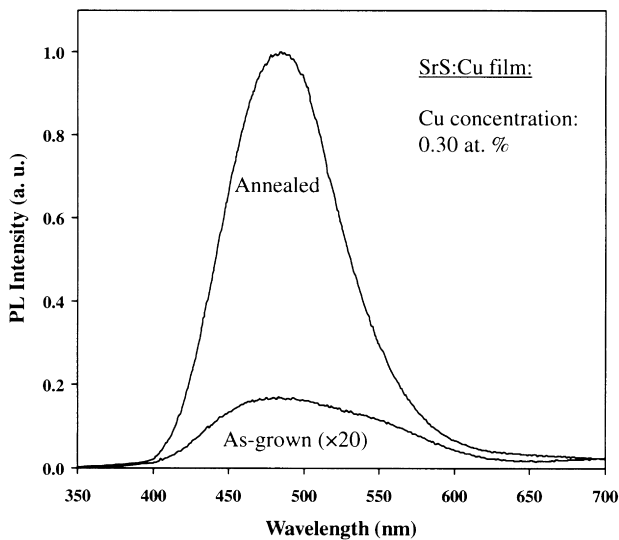


Fig. 2. PL spectra of the as-grown and annealed SrS:Cu films: the PL spectrum of the as-grown film was enlarged 20 times for comparison.

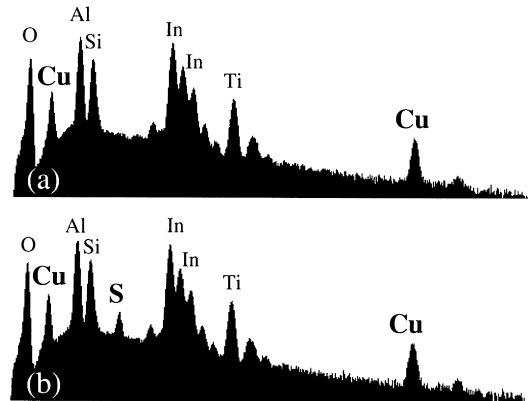


Fig. 3. EDS spectra of the as-grown and annealed films grown by using Cu + H<sub>2</sub>S on ATO/ITO/glass substrate: (a) as-grown; (b) annealed at 750°C for 1 min followed by 650°C for 2 h with H<sub>2</sub>S flow rate of 3.2 sccm.

(SEM), energy dispersive X-ray spectroscopy (EDS), secondary ion mass spectroscopy (SIMS), and photoluminescence (PL) spectroscopy were used to characterize the films. The EL devices were made by sputtering a BaTa<sub>2</sub>O<sub>6</sub> second insulator layer on the SrS:Cu/ATO/ITO/glass substrates followed by e-beam evaporated Al dots as the second contact. The threshold voltage and the luminance  $B_{40}$  at 40 V above the threshold voltage were measured by applying square wave pulses at 60 Hz to the EL devices.

### 3. Results and discussion

A series of SrS:Cu films were studied both as-grown, and after annealing. XRD and SEM studies showed that the films were polycrystalline and that the grain size in the as-grown SrS:Cu films was small (~0.3 μm) and with an angular shape. In situ annealing in the MBE system under a H<sub>2</sub>S atmosphere dramatically improved the crystallinity and the luminescent properties of the SrS:Cu films. Fig. 1 shows the morphologies of the as-grown and annealed SrS:Cu films. It is seen from Fig. 1(b) that the grains became much smoother and the grain size increased to ~2 μm after the annealing treatment. Fig. 2 shows the typical PL spectra for as-grown and annealed SrS:Cu films. The spectrum of the annealed film peaked at 484 nm with CIE coordinates of  $x = 0.160$ ,  $y = 0.278$ . The PL emission of the as-grown film was about 120 times weaker than that of the annealed film, and exhibited a broader spectrum. No EL emission was observed from the as-grown SrS:Cu samples. However, high luminance EL devices were fabricated from the annealed SrS:Cu films. For the optimized Cu concentration of 0.3 at.%, a luminance of  $B_{40} = 26 \text{ cd/m}^2$  at 40 V above threshold with 60 Hz drive was obtained [4]. The CIE coordinates of this sample were  $x = 0.17$ ,  $y = 0.29$ , which was very close to that observed from PL measurement.

In an experiment designed to grow copper sulfide by evaporating Cu in the presence of H<sub>2</sub>S, only a Cu film instead of copper sulfide was obtained. The experiment

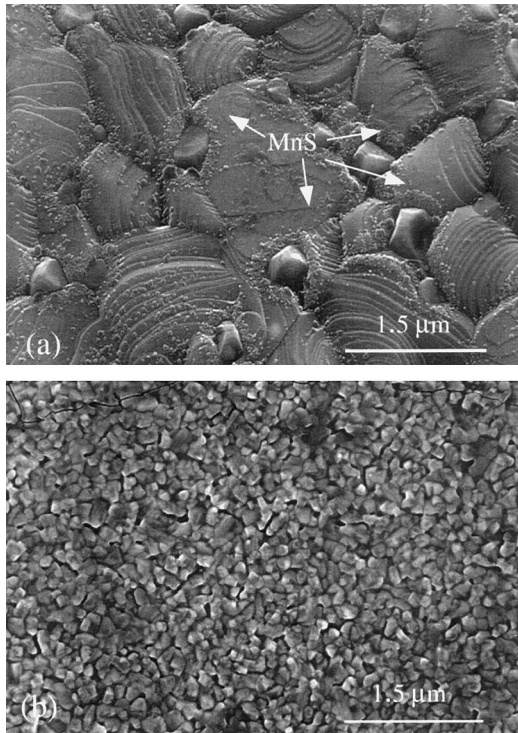


Fig. 4. Morphology of SrS:Cu,Mn films with Cu concentration of 0.6 at.% and different Mn concentrations: (a) 1.8 at.% Mn; (b) 2.6 at.% Mn.

was performed in the MBE system with a Cu flux of  $1.3 \times 10^{-8}$  Torr and a  $\text{H}_2\text{S}$  flow rate of 3.2 sccm. Growth was at  $600^\circ\text{C}$  for 2 h. Fig. 3(a) shows the EDS spectrum of the as-grown film. Only a Cu peak, but no sulfur signal could be detected (in addition, O, Al, Si, In, and Ti were observed from the ATO/ITO/glass substrate). This means that Cu did not react with  $\text{H}_2\text{S}$  during growth at  $600^\circ\text{C}$ . Fig. 3(b) shows the EDS spectrum of the film annealed at  $750^\circ\text{C}$  for one minute followed by 20 min at  $650^\circ\text{C}$  with a  $\text{H}_2\text{S}$  flow rate of 3.2 sccm. Following this anneal a sulfur peak was

detected together with the Cu peak, indicating that Cu was oxidized by  $\text{H}_2\text{S}$  during annealing.

Fig. 4(a) shows the morphology of a SrS:Cu,Mn sample with a Mn concentration of 1.8 at.%. The large grains in Fig. 4(a) exhibited extensive terracing and small precipitates. Large shiny precipitates were observed between these grains. To detect the composition of the grain, EDS studies were therefore performed on these precipitates and within the larger grains. From the EDS spectra, it was found that the Mn concentration in the precipitates was much larger than that within the large grain. By calculating the ratios of Mn/Sr and S/Sr for the different areas, the precipitate was identified to be MnS. From the SEM study on annealed SrS:Cu,Mn films with a Cu concentration of 0.6 at.%, it was found that for low Mn concentrations ( $\leq 1.8$  at.%), large grain sizes ( $\sim 2.0 \mu\text{m}$ ) could be obtained with large precipitates ( $\sim 0.5 \mu\text{m}$ ) at the grain boundaries. When the Mn concentration was higher than 1.8 at.%, only small grain sizes ( $\sim 0.3 \mu\text{m}$ ) were observed. The morphology of a sample with a Mn concentration of 2.6 at.% is shown in Fig. 4(b).

Fig. 5 shows the PL spectra measured for SrS:Cu,Mn samples with different Mn concentrations. For the sample with higher Mn concentration, a single emission peak representative of Mn was observed. However, for the sample containing the same Cu concentration, but a lower Mn concentration, the spectrum showed strong blue and green emissions, respectively. It was found that strong Cu blue emission could only be observed from the samples with Mn concentrations lower than 1.8 at.%. As the Mn concentration became higher than 1.8 at.%, the Cu blue emission became very weak, and the Mn green emission was dominated. EL measurements also showed the same trend. A Cu blue emission was observed for samples with low Mn concentrations and large grain sizes. Only green emission was measured from the samples with higher Mn concentrations.

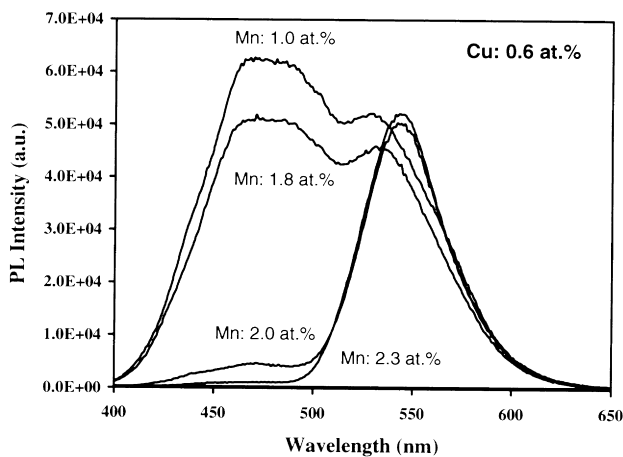


Fig. 5. PL spectra of SrS:Cu,Mn films with Cu concentration of 0.6 at.% and different Mn concentrations.

In the SrS:Cu,Mn system, Mn was oxidized to  $\text{Mn}^{2+}$  during SrS growth, which was confirmed by the observation of bright PL green emission from the as-grown films [3]. As  $\text{Mn}^{2+}$  (0.8 Å) has a much smaller ion radius than that of  $\text{Sr}^{2+}$  (1.13 Å) (the lattice mismatch is 29%),  $\text{Mn}^{2+}$  is very likely to migrate to the grain boundary during annealing. A MnS second phase was therefore formed due to the movement of  $\text{Mn}^{2+}$  along the grain boundary. This migration of  $\text{Mn}^{2+}$  increases the activation energy for the grain boundary movement because the free energy of formation is larger for MnS ( $-214.2 \text{ kJ/mol}$ ) than for SrS ( $-472.4 \text{ kJ/mol}$ ) [5]. Therefore, the migration of  $\text{Mn}^{2+}$  to the grain boundary prevents and pins the grain growth. The oxidation of Cu and the diffusion of  $\text{Cu}^+$  into the SrS lattice reduces the nucleation and boundary layer migration energies and promote the grain growth during annealing in a  $\text{H}_2\text{S}$  atmosphere [2]. These two effects competed with each other. For films with a low Mn concentration, a large grain size and bright Cu blue emission can be obtained resulting from the

oxidation of Cu and the diffusion of  $\text{Cu}^+$  into the SrS lattice. When it behaves as a coating,  $\text{Mn}^{2+}$  migrates to the grain boundary during the grain growth and forms large MnS precipitates as shown in Fig. 4(a). The larger the precipitates, the less effective the pinning of the grain growth [6]. For high Mn concentration, the Mn pinning effect dominates. Very small MnS precipitates or even a MnS thin layer might be formed around the grain boundary to prevent the oxidation of Cu and the diffusion of  $\text{Cu}^+$  into the SrS during annealing. For a grain size of 0.3  $\mu\text{m}$ , a Mn concentration of 1.4 at.% is enough to form a monolayer with a thickness of 5.6 Å (the lattice constant of cubic MnS). This estimation agrees quite well with our experiment results (the critical Mn concentration was around 1.8 at.%) considering that some of the Mn remains in the SrS lattice to produce green emission. The optimized Mn concentration for pure SrS:Mn green emission was determined to be 0.4 at.% [7].

#### 4. Conclusions

The oxidation and diffusion of Cu in SrS:Cu thin film blue phosphors were identified to be the key reasons for the improved crystallinity and luminescent properties upon annealing. Experimental evidence for the oxidation state and diffusion dynamics in the SrS:Cu films has been presented. It was verified that Cu did not react with  $\text{H}_2\text{S}$  during the growth of SrS, but was oxidized during the post-growth annealing process. Also, in the MBE growth of SrS:Cu,Mn, a Mn related second phase was identified at the SrS grain boundaries. Bright  $\text{Cu}^+$  blue emission and larger grain sizes could only be obtained from annealed

samples with low Mn concentrations ( $\leq 1.8$  at.%). For samples with larger Mn concentrations, it is proposed that a second phase MnS layer on the grain boundary might be formed to prevent the ionization of Cu and diffusion of  $\text{Cu}^+$  into SrS lattice during annealing, leading to a weak  $\text{Cu}^+$  blue emission and small grain size. This result confirms the argument that the ionization and diffusion of Cu in SrS are responsible for the improved grain size and electro-luminescent properties in SrS:Cu.

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