Influence of sintering on photoluminiscent emission of SrS:Cu,Ag powders and e-beam evaporated phosphor layers

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Abstract

Recently, SrS:Cu,Ag has been studied by several research groups as a blue emitter for thin film electroluminescent (EL) devices. However, both EL and PL (photoluminescent) spectra of these thin film phosphors suffer from severe non-reproducibility. In order to solve this problem, the effect of sintering the deposition source material (in N2 and H2S) on the PL characteristics of both this source material and the deposited thin films is studied. It will be shown that sintering SrS:Cu,Ag in H2S enhances blue Ag emission in thin films, which is normally partly quenched at room temperature. Sintering also drastically increases the reproducibility of the emission spectra. In order to understand the underlying physical changes, optical and structural/morphological characterizations were performed. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since its rediscovery in 1997 by Sun et al. [1], SrS:Cu (codoped with several elements) has been investigated quite thoroughly as a possible blue electroluminescent (EL) emitter. Especially SrS:Cu,Ag has gained much interest, as its emission color can be true blue. This is presumably caused by activation of the Ag emission due to energy transfer from Cu1 to Ag1 centers [2]. However, the breakthrough of SrS:Cu,Ag is mainly obstructed by a very low reproducibility of the obtained emission spectrum. The Ag emission, which accounts for the blue emission, is often strongly quenched at room temperature [3,4].

Except for the study of powder luminescence, the preparation of powder source materials is often not described. In this work, the effect of sintering the source material for e-beam evaporation on both this source material and the corresponding thin film phosphors is studied. It will be shown that pre-treatment of SrS:Cu,Ag powder at high temperature (sintering) in H2S atmosphere causes a shift in quenching temperature for the Ag emission, so that Ag emission is still present at room temperature.

First, the morphology and emission spectra of powders sintered at different temperatures and in different atmospheres are discussed. A similar study of the morphology and the emission spectra of e-beam evaporated thin films will also be presented. Measurements at low temperature illustrate the shift in quenching temperature of the Ag emission. Finally, the correlation between crystal orientation and sintering atmosphere is reported.

2. Specimen preparation and experimental setup

As pre-treatment, SrS powders (99.9%, CERAC), mixed with metallic Cu (at. conc. 0.4%) and Ag2S (at. conc. 0.6%), were heated in a quartz tube furnace for 2 h. The powders were sintered under a continuous flow (100–150 cm3/min) of nitrogen (N28) or hydrogen sulfide (N25). In order to remove excess oxygen, the tube was thoroughly flushed with nitrogen gas prior to the sintering process. Sintering processes were performed at temperatures ranging from 973 to 1473 K. During sintering in hydrogen sulfide, the H2S dissociated in hydrogen and atomic sulfur; the latter condensed on the cooler parts of the furnace. After passing...
through the furnace tube, the remaining H\textsubscript{2}S was directed to a barrel filled with ZnO, where most of the H\textsubscript{2}S could be chemisorbed (ZnO + H\textsubscript{2}S $\rightarrow$ ZnS + H\textsubscript{2}O). In order to improve safety, the rest gas (partly H\textsubscript{2}S, partly H\textsubscript{2}) was led through H\textsubscript{2}O, making use of the high solubility of H\textsubscript{2}S in H\textsubscript{2}O (300 cm\textsuperscript{3}/100 cm\textsuperscript{3} H\textsubscript{2}O at 293 K). Using the sintered powder, films with a thickness of 900 nm were deposited on Corning 1737 substrates at a substrate temperature of 823 K. A vacuum system (Leybold Univex 450) with a base pressure of $2 \times 10^{-4}$ Pa was used, and depositions were conducted in H\textsubscript{2}S ambient (partial pressure $6 \times 10^{-3}$ Pa). Previous work has shown that reproducible (with respect to structural properties, optical constants and stoichiometric properties) layers are produced in this way [5]. After deposition, the layers were annealed (953 K, 45 min) in a quartz tube furnace in N\textsubscript{2} flow. Spectral information was obtained using an optical multichannel analyzer EG&G OMA III. In PL experiments, the emission from the Ag center strongly depends on the excitation wavelength. It turned out that host excitation was required to obtain strong Ag emission, so only spectra acquired with excitation wavelength of 254 nm will be shown.

Measurements at low temperature were acquired using a cold finger nitrogen flow cryostat with quartz windows. Film crystallinity was checked with a Siemens D5000 XRD (X-ray diffraction) spectrometer (CuK\textsubscript{a} line, stepsize 0.01\textdegree).

3. Results and discussion

3.1. Powders (source material)

Due to technical limitations of the silica tube and the furnace, the maximum temperature used was 1373 K. A study of the pre-treatment temperature and duration

![SEM pictures of SrS:Cu,Ag powder heated in (A) N\textsubscript{2} or (B) H\textsubscript{2}S during 2 h at 1273 K.](image1)

![PL emission spectra of sintered SrS:Cu,Ag powder (1273 K, 2 h) (thin line: RT, thick line: 150 K; A: N\textsubscript{2} sintered powder; B: H\textsubscript{2}S sintered powder).](image2)
revealed that a short exposure (15 min) to relatively low temperature (973 K) is sufficient to obtain both Ag and Cu emission in SrS. Higher temperatures and longer duration make the emission more homogeneous over the powder surface. Under these circumstances, Cu emission often dominates. An optimum pre-treatment process was found to be 2 h at 1273 K. This process is sufficient to activate the dopants homogeneously over the powder, but is less demanding for the sintering setup than pre-treatments at higher temperatures.

Sintering in nitrogen at 1273 K did not cause a considerable volume reduction and grains did not stick together, so that the treated powder still had to be pressed into pellets before electron beam evaporation. Actually, the powder is not sintered in this case. In Fig. 1A a scanning electron microscope (SEM) picture of this unsintered powder is shown. The XRD pattern of the powder showed the presence of SrSO₄. This can be explained by the substitution of sulphur by oxygen, which is present as rest gas in the sintering equipment.

An H₂S atmosphere was found to promote the sintering process, even at relatively low temperatures (973 K). Because of the strong decrease in volume upon sintering, the powder turned into a hard and compact mass so that the sintered powder could be immediately e-beam evaporated, without pressing. The powder mass was reduced with approximately 8% (only 1.5% when pre-heating in nitrogen, under identical conditions), probably due to the removal of adsorbed molecules (sintering during 5 h did not change this mass reduction). Fig. 1B shows a SEM picture of the powder sintered in H₂S. The XRD pattern of the powder did not show any traces of SrSO₄. This is explained by the lack of sulphur deficiency of the powder due to the S-ambient now present in the furnace.

Fig. 2 shows the emission spectra of SrS:Cu,Ag powder sintered in N₂ or H₂S. The emission spectra are shown for both room temperature (rt: thin line) and low temperature (150 K: thick line). At rt, the emission of the powders sintered in H₂S is dominated by Cu emission (emission peaks at approximately 455 and 505 nm). Nor at room temperature, nor at 150 K, blue emission of Ag (at 420 nm) can be seen. Powders which were pre-heated in nitrogen surprisingly showed a bluer PL emission, both at rt and at low temperature. Besides Cu emission, at similar wavelengths as in H₂S sintered powders, emission around 430 nm can be seen, which is thought to be Ag related. In both types of powders, emission at shorter wavelengths gains importance with cooling.

3.2. Thin films

After deposition, the layers were annealed (953 K, 45 min) in a quartz tube furnace in N₂ flow, to increase emission intensity. In contrast with the PL emission from powders, layers made from untreated or N₂ sintered powder hardly show any Ag emission at room temperature. Cu emission accounts almost entirely for the bluish-green photoluminescence (see Fig. 3). Some samples are very green, caused by Cu emission at 525 nm, others are bluish, depending on the importance of the Cu emission at shorter wavelengths.
wavelengths (450–460 nm). Reproducibility in emission spectra is therefore mediocre.

However, in layers deposited from H₂S sintered powder, Ag emission (peak position at 420–425 nm) becomes prominent, so that a deep blue emission (CIE $x = 0.16, y = 0.07$) is achieved (see Fig. 3). Only a small contribution of the Cu emission can be seen. In contrast with the layers evaporated from N₂ sintered powder, the reproducibility was good: strong Ag emission was present in all samples made from H₂S sintered powder.

The total PL intensity of layers made from H₂S sintered powders is lower compared to those made from N₂ sintered powder. However, the PL emission in SrS:Cu,Ag layers made from H₂S-sintered powders is nearly completely Ag emission, and therefore no filters are needed to select the blue emission, as is the case in bluish-green thin films. Also, the emission intensity of SrS:Cu,Ag thin films is several times brighter compared to SrS:Ag layers (both made from powder sintered in H₂S). This again shows the need for copper addition in order to achieve good Ag emission, in agreement with literature [3].

In SrS:Cu,Ag layers made from untreated powder, blue emission depends mostly on the relative importance of the Cu 450 nm center, due to the weaker Ag emission. As stated above, this is in strong contrast with the emission from layers produced out of powder sintered in H₂S, because of the very prominent Ag center at 420 nm, even at room temperature. Fig. 4 shows the PL intensity of the Ag center in layers evaporated from untreated powder (dashed line) and from H₂S sintered powder (full line) as a function of temperature. It can be seen that the quenching temperature for Ag emission is shifted to higher temperatures, allowing considerable Ag emission at room temperature. Cu emission is hardly higher at lower temperatures and is almost completely quenched at 350 K. A possible explanation for the shift in quenching behavior is a small change in the energy levels of the Ag center, due to a different surrounding in the host lattice.

Sintering in H₂S was found to result often in a lower crystallinity (XRD peak area) for e-beam evaporated layers (compared to sintering in N₂). A more significant effect is the change in crystallite orientation. In layers made from untreated or N₂-sintered powder, XRD results show a slightly preferential orientation along [111] or [200]. H₂S sintering of the source material on the other hand enhances the [220] orientation in SrS films. In these layers, the [220]-diffraction peak accounts for 35% of the total reflected intensity, which is considerably more than in the other layers (from untreated or N₂-sintered powder), where the [220]-peak contributes less than 10% to the total intensity.

4. Conclusion

In this work, the effect of pre-heating the source material on the optical and structural properties of the powders and the corresponding thin films was studied. Both heating in N₂ and H₂S leads to activation of emission in powders. Surprisingly, heating in N₂ shows remarkably blue-shifted powder PL as compared to heating in H₂S, where Ag emission is absent. Only the powder heated in H₂S is physically sintered (larger grains).

The effects of heating the source material on the photoluminescence characteristics of thin films are completely different from the effects on powders. In order to obtain Ag emission in SrS:Cu,Ag thin films at room temperature, heating the source material 2 h at 1273 K in H₂S was found to be necessary. The films, evaporated from N₂ sintered powders, did not show significant Ag emission at room temperature. Besides a change in emission properties, the films evaporated from H₂S sintered powder show an increased [220] XRD reflection, whereas all other films showed a [111] or [200] orientation. The presence of the Ag emission at room temperature results from a shift in quenching temperature. More research will be performed in order to understand the physical changes in the films and to explain the discrepancies between PL emission of powders and thin films.

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