Recent progress in the development of full color SrS-based electroluminescent phosphors

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Abstract

A review is given of recent studies on SrS-based phosphors that are being developed for improving the color properties of electroluminescent (EL) displays. A dramatic improvement in the crystallinity, photoluminescence and EL performance for SrS : Cu was achieved by vacuum annealing under a sulfur flow. The two-component SrS : Cu,Ag phosphor has been shown to exhibit an efficient blue color, thus combining the superior excitation properties of Cu with the strong blue radiative properties of Ag. Additionally, studies in improving the EL efficiency by enhancing grain growth and by co-doping are discussed in a new green phosphor, SrS : Mn, and a preliminary results are presented for SrS : Eu. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the past few years significant progress has been made in enhancing the performance of electroluminescent (EL) displays and they are being actively considered for applications in head-mounted and automotive displays. It is expected that full color capability will shortly be available for head-mounted applications, such as active matrix EL displays, and in 1/4 VGA direct view panels, and with significantly higher brightnesses and lower power consumption than current monochrome displays. Many of these advances are a result of recent progress made in EL phosphor technologies.

The development of an optimized EL phosphor is dependent on many variables. Of critical importance is the interaction between the rare earth or transition metal ion activators and the host lattice. This interaction determines the color and luminance of the device. Of secondary consideration for rare earths is the choice of co-activators for charge compensation so as to minimize traps and non-radiative losses. Further considerations can involve substitutional alloying which, by reducing the crystal symmetry and changing the ligand field coupling to the activator, can be used to enhance the luminance and fine tune the chromaticity.
The crystalline quality of the thin films also is critical to maximize the luminance output. Ideally, films with columnar grains up to ~ 2 μm in size are required in these films, which are typically 0.5–1.0 μm thick. This allows efficient excitation of the “hot” electrons and provides internal interfaces to minimize light piping along the film. All of these properties have to be obtained in a single film and ideally grown at low-temperatures so that low-temperature substrates and processes can be utilized. We describe below the progress being made to develop more optimized full color SrS-based EL phosphors.

2. New developments in electroluminescent phosphors

SrS: Cu was first reported as a potential blue electroluminescent (EL) emitter by Kane et al. in 1985 [1]. Recently, Sun et al. prepared SrS: Cu EL devices using magnetron sputtering followed by a 810°C anneal with a significant improvement in 60 Hz luminance at 40 V above the threshold to

\[ L_{40} = 28 \text{ cd/m}^2 \]

with 1931 CIE color coordinates of

\[ x = 0.15, y = 0.23 \]

[2]. The emission of Cu\(^{+}\) centers in alkaline-earth sulfides was identified as a 3d\(^9\)4s\(^0\) (\(^3\)E) → 3d\(^{10}\) (\(^1\)A\(_1\)) intra-ionic transition [3]. The broad emission resulted in significant emission intensity with y-chromaticity below 0.15 for a more saturated blue color compared to SrS: Ce. Their study showed that SrS: Cu was superior to SrS: Ce for the color-by-white approach to full color EL displays. However, a further two-fold increase in EL luminous efficiency is needed for a bright ½ VGA display. Also, a low-temperature process (\( \leq 650\)^oC) is needed so that low-temperature glass substrates can be used to reduce production costs.

2.1. Growth and in situ annealing of SrS: Cu

For the molecular-beam epitaxy (MBE) growth of SrS: Cu a methodology previously used to improve the EL performance of SrS: Ce was used [4]. However, whereas Ag\(^{+}\) was used to compensate Ce\(^{3+}\) doping in SrS and reduce the induced Sr vacancy concentration [5], a series of codoping studies using trivalent ions to substitute on the Sr-site and/or Cl doping on the S-site were investigated to compensate the substitution of Sr\(^{2+}\) with Cu\(^{+}\) and to reduce the charge imbalance induced S vacancies. In addition, other material processes were studied to directly reduce sulfur vacancies.

The SrS: Cu thin films were deposited on glass/ITO/ATO substrates at a rate of 0.1–0.2 μm/h to thicknesses of between 0.3 and 0.6 μm. SrS: Cu was initially grown under high S/Sr ratios as determined from previous SrS: Ce studies [4] at growth temperatures from 500°C to 700°C. The elemental Cu and other solid source materials such as Mn, YCl\(_3\), and Ag were thermally evaporated for the co-doping studies. The Cu flux was varied from \(1 \times 10^{-8}\) to \(1 \times 10^{-6}\) Torr [6]. However, in contrast to the SrS: Ce results, these conditions produced films with a dark brown body color and weak luminescence. Strong photoluminescence (PL) was only observed for samples grown at 700°C but these samples exhibited weak EL emission. Studies using excess S and Mn, Al, YCl\(_3\), and Ag were also conducted, but resulted in little improvement.

A systematic study of post-deposition, in situ vacuum annealing under a sulfur flux was therefore carried out to reduce the native defect density. This was found to dramatically improve both the sample morphology and the EL and PL intensity. Fig. 1 shows the PL intensity versus annealing time for various anneal temperatures and sulfur flow rates. All samples were grown under the same growth conditions at 600°C and annealed for 30 min at 650°C under a 2.5 sccm (N\(_2\) equivalent) t-butyl mercaptan (t-BuSH) flow. As shown, this led to a dramatic increase in the PL intensity by a factor of almost 35, which was attributed to a reduction of sulfur vacancies. For these studies, the best EL performance was obtained for a sample annealed for 60 min with \(L_{40} = 40\) cd/m\(^2\) (1 kHz) and CIE coordinates of \(x = 0.20, y = 0.32\).

Low-temperature PL decay time measurements showed a similar trend, and for a 30 min anneal at 650°C, the 10 K decay time increased from < 20 to 140 μs indicating that non-radiative processes were greatly suppressed by annealing. Furthermore, charge deep level transient spectroscopy (QDLTS) studies also showed a reduction in the sulfur vacancy concentration [7], and after annealing, the...
Fig. 1. Photoluminescence intensity of SrS : Cu as a function of annealing time.

grain size increased from 0.4 to 1–2 μm, as shown in Fig. 2. The white areas in Fig. 2(a) have more than 5 times the Cu concentration of the nonwhite areas as measured by energy dispersive X-ray analysis. These results indicated that Cu precipitation occurs in the as-grown samples, but that annealing eliminated the Cu precipitation and greatly improved the grain size. X-ray diffraction studies also indicated at least twice the (0 0 2) peak intensity for annealed samples as compared with unannealed ones. This improvement in crystallinity and Cu doping uniformity greatly improved the EL performance. Through a further optimization of the growth conditions and by reducing the deposition temperature to 400°C, a 60 Hz EL luminance of $L_{40} = 26 \text{cd/m}^2$ (400 cd/m$^2$ at 1 kHz) with bluer CIE coordinates of $x = 0.17, y = 0.29$ was obtained.

2.2. SrS : Mn thin film phosphors for green electroluminescence

The progress made in developing more efficient blue EL phosphors has led to a need for improved green and red EL phosphors. At present, ZnS : Tb is known to be the most efficient green EL material. However, its efficiency is 2–3 times less than the value ideally required for a bright VGA display. Therefore, the development of an efficient green EL phosphor becomes very important for realizing a full color flat panel display technology. SrS : Mn is a possible candidate as it has exhibited very bright green cathodoluminescence (CL) [8] and photoluminescence (PL) [9] with an excellent chromaticity. However, although not extensively investigated, the EL results reported on thin film SrS : Mn are poor [10]. A study was, therefore, made on this phosphor using a similar methodology as described in Section 2.1.

Structural and optical characterizations for SrS : Mn thin films grown on ATO/ITO/glass showed that the EL emission peaked at 540 nm with CIE coordinates of $x = 0.33, y = 0.64$ but that the grain size was very small (~0.3 μm). In contrast to the PL emission, the 60 Hz EL intensity was very weak with a $L_{40}$ of less than 4.2 cd/m$^2$. The large difference was attributed to the different
excitation mechanisms of PL and EL. In EL devices, “hot” electrons excite the activators and ideally grain sizes greater than 0.5 μm are needed to accelerate the electrons to high enough energy, otherwise they are scattered at the grain boundaries [6]. Because the impact cross section of Mn\(^{2+}\) in SrS is much smaller than in ZnS [11], a higher concentration of “hot” electrons are needed to excite the same number of Mn\(^{2+}\) ions in SrS. Therefore, the poor EL performance of SrS: Mn was attributed to the small grain size.

However, in the study of the MBE growth of SrS: Cu described in Section 2.1, it was found that a large grain size (1–2 μm) could easily be obtained after an in situ post growth annealing [6]. Fig. 3 shows the dependence of grain size on Cu flux showing that Cu is a good nucleation agent to promote grain growth in SrS with a maximum grain size of 1.8 μm being achieved. Therefore, a series of SrS: Mn,Cu samples were grown for Mn fluxes between 3 \times 10^{-9} and 1.2 \times 10^{-7} Torr in combination with the optimum Cu flux determined from this study. Fig. 3(b) shows that, unfortunately, the grain size decreased quickly with increasing Mn flux because of a pinning effect. For \(F_{\text{Mn}} = 1.2 \times 10^{-7}\) Torr, which is close to the optimum Mn flux for pure SrS: Mn, the average grain size decreased to 0.5 μm, compared to 0.3 μm grains for the SrS: Mn samples. The surface morphologies also changed due to the addition of Mn. There are many small particles at the grain boundaries, and the grain boundary structure shows more curvature compared with that of pure SrS: Cu (Fig. 3 inset). The concentration of small particles also increased with the Mn flux and therefore were identified as being associated with Mn\(^{2+}\) and also responsible for pinning the grain size. The Mn pinning effect is well understood in the field of metallurgy and is used to obtain fine-grain alloys [12,13]. It was shown that second phase particles on the grain boundary play the major role in this effect [14]. In the case of SrS: Mn,Cu, Mn\(^{2+}\) has a smaller ionic radius (0.8 Å) than Sr\(^{2+}\) (1.13 Å) and a higher surface mobility [4]. It can therefore easily migrate to the grain boundaries during growth and form second phase particles. These particles reduce the grain boundary area and lower the driving force for grain growth. EL devices were fabricated and measured for SrS: Mn,Cu samples with the optimum \(F_{\text{Cu}}\) as a function of Mn flux. The Mn\(^{2+}\) green EL emission dominated for \(F_{\text{Mn}} \geq 1.1 \times 10^{-8}\) Torr. For \(F_{\text{Mn}} = 1.1 \times 10^{-8}\) Torr, the 60 Hz \(L_{40}\) was 5.4 cd/m\(^2\) with CIE coordinates of \(x = 0.31, y = 0.53\), compared to no detectable EL for SrS: Mn samples with the same growth and annealing conditions. The increase in brightness is attributed to the larger grain size compared with that for the pure SrS: Mn sample. The Mn\(^{2+}\) emission intensity did not increase significantly with increasing Mn flux, possibly because the increased concentration of Mn\(^{2+}\) activators was offset by the reduced grain size due to the Mn pinning effect. However, a greatly improved 60 Hz EL performance of \(L_{40} = 71\) cd/m\(^2\) with an efficiency (\(\eta_{40}\))
of 0.43 lm/W, was obtained for a 400°C deposition and a post-deposition in situ vacuum anneal similar to that used for the SrS: Cu process.

2.3. Growth and characterization of SrS: Cu, Ag

As a result of the breakthrough in obtaining efficient EL emission with a good blue chromaticity from SrS: Cu [2,3,15], attention was directed to a similar system, SrS: Ag, which exhibits a highly saturated blue PL and cathodoluminescence emission centered at 430 nm. However, the EL intensity was found to be very weak [16] which was attributed to poor EL excitation efficiency. Therefore, attempts were made to improve the EL performance of SrS: Ag by co-doping with Cu. In this two-component system, the high excitation efficiency of Cu and the high luminescence efficiency of Ag are combined to produce highly efficient EL with superior blue chromaticity. The use of two different types of ions for high excitation efficiency and desirable color adds great flexibility to phosphor development. However, the successful sensitization depends critically on efficient coupling between the Cu sensitizer and the Ag activator. The luminescence characteristics of SrS: Cu,Ag were, therefore, investigated to precisely probe the interaction between the Cu and Ag ions to ascertain the efficiency of the coupling between the two ions [17].

As shown in Fig. 4, SrS: Cu,Ag exhibits a deep blue color at 300 K with a peak emission at 2.876 eV (430 nm) and a line width of 390 meV, providing a highly saturated blue CIE color coordinates of $x = 0.165, y = 0.088$. As the temperature was decreased to 10 K, the emission band did not shift and two additional emission bands were observed at 3.443 and 2.398 eV. Comparisons with the low-temperature PL spectra of singly doped SrS: Cu and SrS: Ag showed that the two peaks at 3.443 and 2.876 eV were emissions from Ag and the 2.398 eV peak was emission from Cu. This assignment was also supported by the temperature dependence of these emission bands in singly doped SrS: Ag and SrS: Cu samples; the two Ag emission bands were independent of temperature whereas the Cu emission exhibited a large blue shift with increasing temperature [18].

Similar PL properties were also found for various Ag concentrations with a fixed Cu concentration. Fig. 5 shows the main emission peak position and PL intensity as a function of the concentration ratio, Ag/(Cu + Ag). It is clear that the main emission band shifts from the Cu emission band to the Ag emission band when the concentration ratio exceeds 0.44. The Ag emission intensity also increased with increasing Ag/(Ag + Cu) concentration ratio and at a ratio of 0.62 exhibited a five-fold enhancement compared to singly doped SrS: Ag, before decreasing at higher Ag/(Ag + Cu) concentration ratios. On the other hand, the Cu emission intensity monotonically decreased as the Ag/(Ag + Cu) concentration ratio was increased and at a concentration ratio of 0.62 it was reduced by a factor of 2, compared to the singly doped SrS: Cu. This enhancement of the Ag emission and the simultaneous suppression of the Cu emission in the SrS: Cu,Ag samples are indicative of energy transfer from Cu to Ag. In further support of the energy transfer model, the photoluminescence excitation (PLE) measurements showed that the Cu excitation bands appeared in the excitation spectra of the Ag emission band, directly confirming energy transfer between the Cu and Ag ions [19].
EL characterizations were also consistent with the PL study and it was evident that the emission from SrS:Cu,Ag originated from the same center as the singly-doped Ag system. Typical 60 Hz EL results for sputtered SrS:Cu were $L_{40} = 34 \text{ cd/m}^2$ at $x = 0.16$, $y = 0.24$ and $\eta_{40} = 0.25 \text{ lm/W}$, and for sputtered SrS:Ag, $L_{40} = 0.3 \text{ cd/m}^2$ at $x = 0.17$, $y = 0.16$ with $\eta_{40} = 0.001 \text{ lm/W}$, whereas sputtered SrS:Cu,Ag yielded $L_{40} = 27 \text{ cd/m}^2$ at $x = 0.17$, $y = 0.15$ and $\eta_{40} = 0.25 \text{ lm/W}$. To gain greater insight into this sensitization mechanism, detailed electrical characterizations were performed [20]. It was found that SrS:Ag exhibited nearly ideal capacitance (C–V) characteristics with no capacitance overshoot near the threshold voltage. From internal charge-phosphor field ($Q-F_p$) measurements, the total transferred charge at 40 V above threshold was evaluated to be 76 nC. Also, no trailing edge emission was observed in SrS:Ag for voltages as high as 60 V above threshold. Thus, there is no localized space charge generation in the phosphor. However, contrasting behavior was observed from the singly doped Cu and Cu–Ag co-doped samples, as shown in Fig. 6. Both SrS:Cu and SrS:Cu,Ag exhibited a large capacitance overshoot in their C–V curves and the $Q_{\max}-V_{\max}$ curves yielded higher capacitances of 3.7 and 2.6 nF, respectively, in contrast to the measured insulator capacitances of 2.2 nF for these devices. Both SrS:Cu and SrS:Cu,Ag also exhibited a trailing edge emission which increased in magnitude with increasing applied voltage, indicating that the Cu centers were ionized. These factors indicated that space charge was generated by the ionization of Cu and then localized within the phosphor. Analysis shows that the space charge density, $N_{sc}$, was $\sim 5.5 \times 10^{16} \text{ cm}^{-3}$ in SrS:Cu,Ag which agrees very well with the values obtained for SrS:Cu ($N_{sc} = 6.2 \times 10^{16} \text{ cm}^{-3}$). Due to the ionization of Cu, the charge transferred in the singly SrS:Cu and SrS:Cu,Ag samples (163 and 154 nC, respectively) was approximately twice that for the singly doped SrS:Ag (76 nC). Since the space charge and the transferred charge were approximately the same for both the singly Cu doped and Cu–Ag co-doped samples, the charge injection and transport properties were concluded to be independent of Ag doping and to be dominated by Cu. However, the radiative (emission) characteristics were due to the Ag center, showing that energy transfer from Cu to Ag also occurred under EL excitation.
From the above results, the excitation properties of SrS:Ag,Cu systems are dictated by the Cu centers, whereas the radiative properties are governed by the Ag centers. It is the energy transfer process which provides the bridge between Cu ions and the emitting ions. The conventional “single-component” phosphors are limited in that the activator must be efficient both in its excitation and radiative properties, restricting the number of efficient activators with the desired chromaticity for full color displays. However, these criteria can more easily be met for “two-component” phosphors. The activator should exhibit the desired color in the chosen host lattice and have a good radiative efficiency to maximize the luminescence. The sensitizer must have a large excitation cross-section to maximize the excitation efficiency. Of course, the success of this technique hinges on the strength of the energy transfer from the sensitizer to the activator ion. Successful sensitization of SrS:Cu,Ag opens up the possibility of designing and developing a new class of two-component EL phosphors that exhibit both superior color and excitation efficiency than conventional single-activator EL phosphors.

2.4. SrS: Eu red EL phosphor

Encouraged by the success of SrS systems for blue and green emission, studies were extended to obtain an efficient red phosphor. SrS:Eu is a red emitting phosphor with an emission band centered at 610 nm giving CIE chromaticity coordinates of $x = 0.600, y = 0.395$. As Fig. 7 shows, however, the typical luminance and efficiency for this material are rather poor with $L_{40} = 5 \text{ cd/m}^2$ and $\eta_{40} = 0.017 \text{ lm/W}$.
3. Summary

A review has been given of new developments in SrS-based EL phosphors. It was demonstrated that a low-temperature (650°C) sulfur anneal enhances the blue EL emission from MBE SrS:Cu phosphors. PL, decay time, QDLTS measurements and SEM studies indicated a great improvement in crystallinity, a large reduction in the sulfur vacancy concentration, and a large increase in the grain size due to the sulfur annealing process. The concept of a two-component phosphor has been introduced in which the superior excitation properties of a co-activator (Cu) have been coupled to the desired radiative properties of the activator (Ag). The strong energy transfer that occurs between these two ions has resulted in a new blue phosphor that significantly enhanced the color coordinates of EL displays. The success of the two-component phosphor approach opens a new pathway to the development of highly efficient EL phosphors with saturated color chromaticity. It has also been demonstrated that Cu can produce significant grain growth in SrS. However, in the development of a SrS-based green phosphor, a Mn pinning effect was observed which restricted the grain size to less than 0.5 μm and which limited the EL performance. Traditional growth and process methods were not effective in overcoming the pinning problems, and thus, new techniques are needed to improve the brightness and efficiency of Mn-activated SrS EL phosphors. The potential of applying these techniques to other SrS-based phosphors is expected to result in a full color RGB set.

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