

Blue- and green-emitting SrS:Cu electroluminescent devices deposited by the atomic layer deposition technique

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Observed structural, compositional, and optical differences between blue- and green-emitting SrS:Cu thin films deposited by the atomic layer deposition technique were studied. The use of hydrogen in the deposition process resulted in green-emitting electroluminescent devices. The green-emitting devices had also the highest potassium (K) content, but the exact role of K was not resolved. The green emission is thought to originate from copper pairs and isolated off-centered copper ions at octahedral sites, whereas blue emission is suggested to originate from copper ions at tetrahedral interstitial sites. The brightest blue-emitting device, measured at 60 Hz, emitted 17 cd/m² at 40 V above the threshold voltage (L_{40}) with $x=0.17$ and $y=0.30$ as the Commission Internationale de l'Eclairage color coordinates. Conversely, the brightest green-emitting device emitted 44 cd/m² with $x=0.33$ and $y=0.58$. The blue- and green-emitting devices also showed different time-resolved electroluminescence behavior, which suggests reduced dynamic space charge within the green-emitting phosphors resulting in the higher emission intensity in the green-emitting devices. © 2003 American Institute of Physics. [DOI: 10.1063/1.1603349]

I. INTRODUCTION

A lack of deep and bright blue emission has been a major obstacle for the commercialization of full color alternating current thin-film electroluminescent devices. The phosphor candidates SrS:Cu and BaAl₂S₄:Eu have been considered as the best sources of blue emission in flat panel displays.^{1,2} The europium-doped BaAl₂S₄ thin films have been deposited only by an electron-beam evaporation (EBE) method. Since then, atomic layer deposition (ALD, earlier named atomic layer epitaxy),³ chemical vapor deposition (CVD),⁴ EBE,⁵ hot wall deposition,⁶ molecular-beam epitaxy (MBE),⁷ pulsed laser deposition,⁸ reactive evaporation,⁹ and sputtering¹⁰ have also been used for the deposition of the SrS:Cu thin films.

Earlier studies have shown that the introduction of hydrogen during EBE, CVD, and sputtering processes can result in improved emission intensity in SrS:Ce, Eu, SrS:Cu, and CaS:Eu phosphors, respectively.^{4,11,12} It was suggested that the underlying reasons included a decreased amount of

oxygen in the films, as well as both enhanced crystallinity and better stoichiometry.^{4,11,12} However, a preliminary ALD study showed that a supply of hydrogen during the SrS:Cu ALD process resulted in green emission.¹³ Both blue and green emission from the SrS:Cu films has also been observed earlier but the exact reasons for the different emission colors were not known.^{3,9,14} In this study, blue-emitting SrS:Cu thin films were deposited by a standard nonhydrogen ALD process, while green-emitting SrS:Cu thin films were grown using a hydrogen supply during the ALD process. The samples were characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM), secondary ion mass spectroscopy (SIMS), time-of-flight elastic recoil detection (TOF-ERD), x-ray diffraction (XRD), and electrical, electroluminescence (EL), and photoluminescence (PL) measurements to study the differences between blue- and green-emitting SrS:Cu thin films, and propose reasons for the different emission colors.

II. EXPERIMENTS

Insulators and phosphors were deposited using ALD.¹⁵ The underlying EL device structure consisted of a Corning1737 glass/ITO/Al_xTi_yO_z/SrS:Cu/Al₂O₃/Al stack.

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The deposition temperature of the phosphor was 300 °C. The precursors Sr(thd)₂ (thd=2,2,6,6-tetramethyl-3,5-heptanedionato), Cu(thd)₂, and H₂S were used as the Sr, Cu, and S sources, respectively. N₂ was used as a carrier and purging gas. The samples were annealed at 725 °C for about 7 h before analyses. The upper insulator was deposited after annealing. However, the samples that underwent AFM, SEM, SIMS, TOF-ERD, and XRD analysis were not covered with an upper insulator. The green-emitting devices were deposited in the same way as the blue-emitting devices except that a gas mixture of N₂ and H₂ (92% N₂ and 8% H₂) was pulsed into the reactor during SrS:Cu deposition. The gas mixture was fed into the reactor via a separate source tube and the hydrogen content in the total gaseous flow was 3%. In general, hydrogen was pulsed in every ALD cycle during the deposition of the green-emitting samples. When supplied after the Sr(thd)₂ and Cu(thd)₂ pulses, hydrogen was pulsed after the purging pulses of the Sr and Cu sources. When supplied after the H₂S pulse, hydrogen was pulsed before the purging pulse of H₂S. The blue-emitting devices in this study were categorized as samples with $x=0.2$ and $y=0.3$ as the Commission Internationale de l'Éclairage 1931 color coordinates, whereas the green-emitting devices were with $x=0.3$ and $y=0.6$.

Film thicknesses were evaluated by fitting reflectance spectra. The spectra were measured in the wavelength region of 400–1100 nm. Corresponding thicknesses of the SrS:Cu films were between 720 and 950 nm depending on sample type and measurement point. Film crystallinity was examined with XRD using Cu $K\alpha$ radiation and Ni filter (Philips MPD 1880, Eindhoven, The Netherlands). SEM investigations of the film surface morphology employed a Zeiss (Oberkochen, Germany) DSM 940 microscope using a 20 keV primary electron beam. AFM measurements were carried out in air in contact mode (ThermoMicroscopes Auto-Probe CP Research, Sunnyvale, CA). Root-mean-square (rms) roughness values were determined from AFM images using the software of the microscope.

The elemental depth profiles of the films were determined with a TOF-ERD analysis using a beam of 53 MeV ¹²⁷I¹⁰⁺ ions obtained from an EGP-10-II tandem accelerator.¹⁶ The recoiled atoms were detected at an angle of 40° and the sample was tilted 20° relative to the beam direction. In TOF-ERD analysis, both the velocity and energy of the recoils are measured and, therefore, different masses can be separated and elemental energy spectra obtained. These energy spectra are converted to depth profiles on the basis of the measurement geometry, elastic scattering cross sections, and stopping powers. The reported elemental contents were always integrated from the middle of the sulfide films to minimize the influence of the oxide layers above and below. The compositional characteristics of the samples were also analyzed by negative and positive ion dynamic SIMS. Dynamic SIMS was utilized to document dopant and impurities levels and their distribution throughout the film. SIMS analysis was carried out on a Physical Electronics (Chanhassen, MN) PHI 630, using a 7 keV O⁺⁺ source with a current of 150 nA, on an analysis area of 600

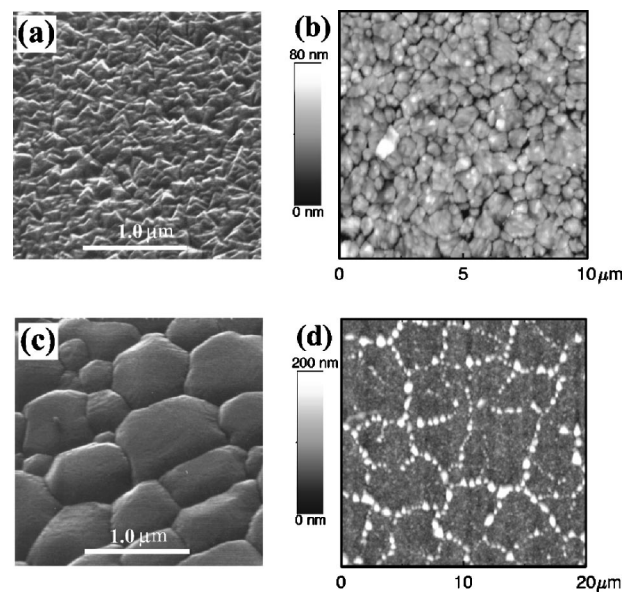


FIG. 1. (a) SEM image of the blue-emitting sample with 0.11 at. % Cu and a luminance L_{40} of 7 cd/m². (b) 10×10 μm top view AFM image of the blue-emitting sample with 0.15 at. % Cu and a luminance L_{40} of 17 cd/m². (c) SEM image of the green-emitting sample with 0.14 at. % Cu and a luminance L_{40} of 19 cd/m². (d) 20×20 μm top view AFM image of the green-emitting sample with 0.22 at. % Cu and a luminance L_{40} of 44 cd/m². Cu contents were calculated using a TOF-ERD analysis.

×600 mm (50% gate). Charge neutralization was accomplished utilizing a 2.0 keV electron beam.

PL measurements were performed using an argon-ion laser (Spectra-Physics, Mountain View, CA, BeamLok 2085) with 275 nm single line optics. The laser power was reduced to an appropriate level by using a set of neutral density filters to avoid local heating. Typical excitation intensities were between 50 mW/cm² and 50 W/cm². The PL signal was then dispersed by a monochromator (Spex 1000M, Edison, NJ) and detected by a thermoelectrically cooled GaAs photomultiplier tube operating in the photon counting mode. For PL excitation (PLE) measurements, a 450 W Xe lamp coupled with a small monochromator (Spex 1681, Edison, NJ) was used as a tunable excitation source. Time-resolved PL measurements were performed by using an optical parametric oscillator (Spectra-Physics MOPO 730-10) pumped by a frequency-tripled Nd:YAG laser (Spectra-Physics GCR 230-10), which is tunable from 220 nm to 1.8 μm and has a pulse width of approximately 8.5 ns. The samples were mounted in a temperature variable cryostat where the temperature can be controlled from 10 K to 300 K.

Fresh EL devices were aged for 20 h at 500 Hz near a threshold voltage before electro-optical measurements that were made at 60 Hz using a trapezoidal wave form. The threshold voltage was defined to be a point where the device emitted 1 cd/m². EL spectra were measured with a Photoresearch (Chatsworth, CA) PR650 spectrometer.

III. RESULTS

A. Morphological and structural studies

Figure 1 shows selected AFM and SEM images of the

blue- and green-emitting samples. In this respect, it seems that grain size, Cu content, and EL intensity are all interrelated, although no direct correlation could be identified with the emission color. This is in agreement with an MBE study where blue-emitting SrS:Cu devices were studied.⁷ Large grain size was explained to be necessary to permit the electric field to accelerate electrons to high energies before they are scattered at grain boundaries, a necessary step given the need for sufficient high-energy “hot” electrons to excite the activators to achieve a high luminance.⁷ The sample shown in Fig. 1(d) seems to contain a continuous network of flat areas (rms > 10 nm) that are surrounded by grains having heights exceeding 100 nm in many places. Unfortunately, it was difficult to analyze whether the flat areas are continuous or consist of several grains that are over 1 μm in a diameter. The main reason for the high luminance of this sample could be attributed to the large grain size that is induced by the high amount of copper. Similar cracking as in Fig. 1(d) has also been observed by Poelman *et al.*,¹⁷ who used EBE as a deposition method. The most probable reason for these and other cracks seen in the course of this study is the annealing at high temperatures.

XRD measurements showed reflections only from the (111) and (222) crystal planes of the cubic SrS. Full width at half maximum values of the (111) diffraction peaks were 0.11° or 0.12° indicating that most of the crystallites were quite large in all the samples studied.

B. Impurity analysis

SIMS results showed that the concentration of K was higher in the green- than blue-emitting samples, while the blue-emitting samples contained slightly more Cl than the green-emitting samples. When the blue- and green-emitting samples were examined separately, the higher amount of Na and the lower amounts of C and O seemed to correlate well with the higher EL intensity.

Impurities in the interior of the sulfide films were analyzed by TOF-ERDA. The results showed that the C, H, and O concentrations were, respectively, 0.1–0.2 at. %, 0.2–0.4 at. %, and 0.2–0.7 at. % without any correlation to the emission color. A low amount of oxygen in the blue-emitting samples seemed to correlate well with the high EL intensity, as supported also by the TOF-ERD analysis. This finding could not be verified with the green-emitting samples because some green-emitting samples were protected by an Al_2O_3 layer, which can induce interference signals in the TOF-ERD measurements and increase the value of the measured oxygen content.¹⁸ Traces of K were detected in some green-emitting samples also by TOF-ERD but the K signal was so low that the K content could not be determined reliably. In other words, the concentration of K was well below 0.1 at. %. The strong signal from S shadowed a possible Cl signal, and Na was not detected. In the earlier ALD studies, SrS films have been protected with a passivation layer before any impurity analysis because unprotected SrS reacts with air, resulting in a high concentration of impurities.^{18,19} In this work, the passivation layer was not used, and the amounts of C, H, and O were, thereby, the maximum values. However,

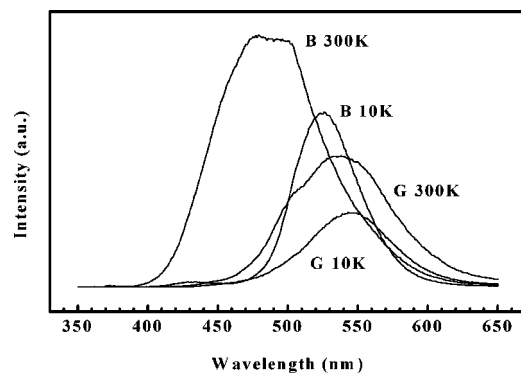


FIG. 2. PL spectra of the deepest blue- (B) and green- (G) emitting samples measured at room temperature and 10 K. Excitation wavelength was 275 nm. The spectra are not in the same scale.

the low levels of impurities in this study indicated that the high-temperature annealing has passivated the surface of the SrS films quite well and the main sources for the impurities were believed to be Sr and Cu precursors.

C. Photoluminescence and decay time measurements

Figure 2 shows PL spectra of the deepest blue- and green-emitting samples at room temperature and 10 K. The blue-emitting sample has a blue emission at ~ 480 nm and a green emission at ~ 525 nm at 300 and 10 K, respectively. Alternatively, the green-emitting sample has a green emission at ~ 535 and 545 nm at 300 and 10 K, respectively. The broad shape of the spectra suggests that they probably consist of two or more peaks. The blue emission part of the spectrum is quenched at 10 K and can hardly be seen in the spectrum of the green-emitting sample even at room temperature. The excitation spectra of these samples were measured at 10 K and are shown in Fig. 3. The blue-emitting sample (green at 10 K) has a host excitation of SrS at 265 nm and a direct excitation of Cu^+ at 280 and 310 nm, whereas the green-emitting sample has peaks at 265, 310, and 360 nm. The peak at 360 nm is probably an indication of Cu^+ pairs.²⁰ The decay profiles in these samples are shown in Fig. 4. The fast component in the decay curve of the blue-emitting sample is almost invisible, while the decay time of the slow component is ~ 190 μs . Alternatively, the decay

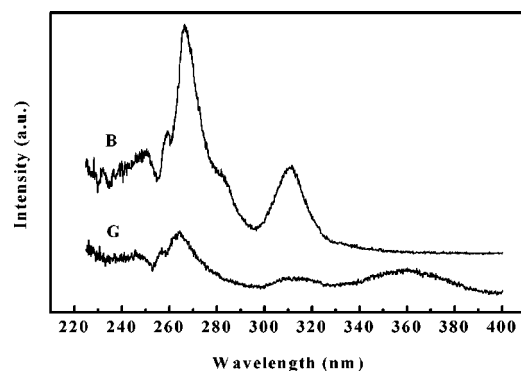


FIG. 3. PLE spectra of the deepest blue- (B) and green- (G) emitting samples measured at 10 K. Emission wavelengths of 525 nm (B) and 546 nm (G) were monitored.

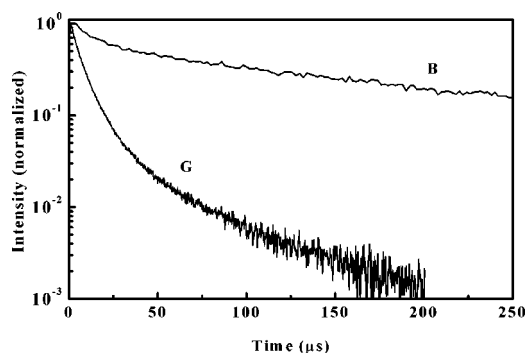


FIG. 4. PL decay curves of the deepest blue- (B) and green- (G) emitting samples measured at 10 K. Emission wavelengths of 525 nm (B) and 545 nm (G) were monitored.

curve of the green-emitting sample can be fitted to fast and slow components with decay times of $<10 \mu\text{s}$ and $\sim 40 \mu\text{s}$, respectively.

In general, all of the samples emitted green light at 10 K. Also, the excitation spectra of different samples were otherwise similar, except for the green-emitting samples exhibiting a peak at $\sim 360 \text{ nm}$. The green emission in SrS:Cu films and powders at low temperatures is well studied,^{3,9,20,21} but the exact reason for the different emission color at different temperatures has not yet been resolved (cf. Sec. IV). However, the higher peak intensity at 310 nm than at 280 nm in the excitation spectrum, i.e., the ${}^1A_{1g} \rightarrow {}^1E_g$ transition exhibiting a higher intensity than the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition, suggests that the ground-state isolated Cu^+ ion is at the off-centered octahedral site.^{3,22} The excitation peak at 360 nm has not always been seen in the other studies of green-emitting samples, which implies that there are probably other reasons for the green emission than just Cu pairs.

Decay curves of all the samples could be subdivided into fast and slow components. The decay times for the slow component were between 130 and 190 μs , except for the green-emitting sample shown in Fig. 4. Typically, it has been thought that a high dopant content, small grain size, low symmetry, increased defect density, and high amount of dopant pairs/agglomerates decreases the decay time.²³ In this study, smaller grain size seemed to lower the decay time for both the blue- and green-emitting samples. In addition, the green-emitting samples seemed to decay somewhat faster than the blue-emitting samples. This behavior can be related to the lower symmetry and higher concentration of pairs within the green-emitting samples. The pronounced excita-

tion peak at 360 nm, along with the very fast decay of the green-emitting sample shown in Figs. 3 and 4 may indicate that the amount of copper pairs is relatively high in this particular sample. As the PL results of this study are compared to those from an earlier ALD study on SrS:Cu films,³ the only distinct difference is that the green-emitting samples in this study have a peak at 360 nm in their excitation spectra. On the other hand, the only difference between the deposition conditions was the use of H_2 pulsing during the deposition of the green-emitting samples in this work, which could imply that the H_2 pulsing enhanced the formation of copper pairs (cf. Sec. IV).

D. Electro-optical measurements

Table I shows the electro-optical data of selected blue- and green-emitting devices after aging. It can be seen that the green-emitting devices are more efficient, have higher luminance, and transfer less charge than the blue-emitting devices. When the blue- and green-emitting devices are compared separately, the luminance seems to depend on Cu content and grain size but not on film thickness (cf. Sec. A). The latter only affected the threshold voltage of the devices. In the earlier studies, maximum luminances were achieved with higher Cu concentrations than those used in this study. Nevertheless, it is probable that the luminance of the blue-emitting samples would saturate to lower values than the luminance of the green-emitting samples because the best green-emitting devices have been brighter than the best blue-emitting devices even in the earlier studies.^{1,14}

Transient luminance [$L(t)$] analysis showed a strong trailing edge emission (TEE) in the blue-emitting samples but a quite weak TEE in the green-emitting samples, as shown in Fig. 5. In literature, the existence of the TEE has been considered as an indication of dynamic space-charge formation and impact ionization mechanism within the phosphor.²⁴ The double-peak nature of the TEE was found only in the blue-emitting devices. However, it is difficult to say if the both peaks are present also in the green-emitting devices because of their overall low TEE. In the recent study of SrS:Cu, Ag by Singh *et al.*,²⁵ it was suggested that the first and second peaks in the TEE are caused by the release of electrons from the bulk traps and shallow interface states, respectively. These electrons recombine radiatively with the nearby ionized activators as the voltage drops.²⁵ The smaller fraction of TEE in the green-emitting devices suggests that the amount of the dynamic space charge was lower as com-

TABLE I. Electro-optical data of the selected devices. The data were measured at 60 Hz after aging. The threshold voltage (U_{thr}) is defined by emission of 1 cd/m^2 . Luminance (L_{40}), transferred charge (Q_{40}), and efficiency (η_{40}) were measured at 40 V above threshold.

| Emission | U_{thr} (V) | L_{40} (cd/m^2) | Q_{40} ($\mu\text{C/cm}^2$) | η_{40} (lm/W) | Color coordinates | | EL peak wavelength (nm) |
|----------|-------------------------|---------------------------------|------------------------------------|----------------------------------|-------------------|------|----------------------------|
| | | | | | (x,y) | | |
| Blue | 137 | 7 | 1.4 | 0.08 | 0.15 | 0.25 | 468 |
| Blue | 107 | 17 | 1.6 | 0.21 | 0.17 | 0.30 | 484 |
| Green | 133 | 19 | 1.3 | 0.25 | 0.29 | 0.58 | 540 |
| Green | 124 | 44 | 1 | 0.79 | 0.33 | 0.58 | 552 |

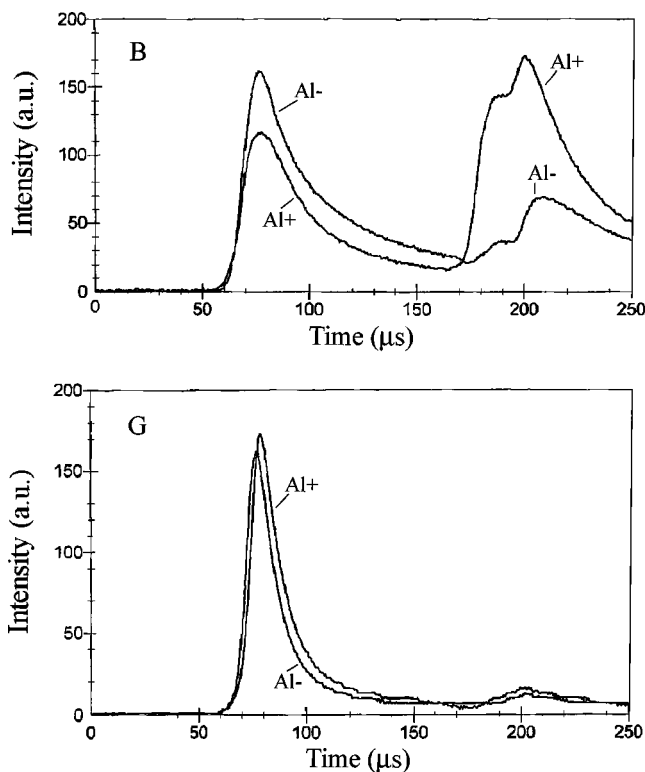


FIG. 5. Time-resolved EL of the brightest blue- (B) and green- (G) emitting devices.

pared to the blue-emitting devices, and could thus be the primary reason for the higher luminance of the green-emitting devices.¹⁴ The $L(t)$ analysis showed also that the polarity dependence of the emission was more pronounced in the blue- than in the green-emitting devices (Fig. 5). This observation may indicate that in the green-emitting samples, the Cu ions are more evenly spread close to the interfaces and/or that in the blue-emitting devices, the electron supply is different at the two interfaces.^{26,27}

IV. DISCUSSION

Blue and green emission in SrS:Cu films and powders has been reported numerous times in literature. While the emission color has always been green at lower temperatures, both blue and green emission has existed at room temperature. However, there are discrepancies concerning the exact nature of the emission centers. Recently, Wruck *et al.*⁹ proposed that at low temperatures practically all Cu^+ ions are paired around a Sr vacancy and the pairs are the reason for the green emission at low temperatures. On the other hand, both Yamashita *et al.*²⁰ and Li *et al.*³ have suggested that both isolated and paired/aggregated Cu^+ ions can emit green color. Based on their own and earlier Cu^+ -doped alkaline halide²² PL studies, they proposed that the isolated green-emitting Cu^+ ion is off centered at low temperatures, which is supported also by the PL measurements in this study.

The oxidation state +2 is very common in copper compounds. It is therefore possible that the Cu^{2+} oxidation state is also present in this study. Earlier ALD studies on Cu_xS depositions, using the same Cu^{2+} precursor than in this

study, have shown that the CuS phase can be deposited only below 225 °C, while Cu_2S was obtained at higher temperatures.^{28,29} This finding, together with the PL analysis, suggest that copper ions in the SrS are mainly in the oxidation state +1, which results in a charge mismatch that is compensated by defects like impurities and/or vacancies. In the study by Wruck *et al.*,⁹ the existence of Sr vacancies was proposed, but formation of S vacancies is believed to be more probable.^{3,30} It has been suggested that a Cu^+ ion with an adjacent S vacancy emits green light, while blue emission arises from a six-fold-coordinated Cu^+ site.³⁰ This suggestion was studied by codoping SrS:Cu powder with Y^{3+} and/or Na^+ and observing that the Na^+ codopant enhances the green emission probably by increasing the number of S vacancies and five-fold-coordinated Cu^+ sites, whereas the Y^{3+} codopant balances the charge mismatch and enhances the blue emission probably by decreasing the concentration of S vacancies and five-fold-coordinated Cu^+ sites.³⁰ It was suggested that the same behavior could also apply to other M^+ and M^{3+} codopants.³⁰ On the other hand, chlorine doping has also been found to enhance blue emission,³¹ and it has been suggested that Cl_S reduces the number of S vacancies.³ However, if the $\text{Cu}-\text{V}_\text{S}$ complexes are the main reason for the green emission, the six-fold-coordinated blue-emitting Cu^+ sites should turn to five-fold-coordinated, be nonradiative, or transfer energy to the five-fold-coordinated sites at low temperatures.

As an alternative explanation for the blue emission at room temperature, both Li *et al.*³ and later Wruck *et al.*⁹ proposed a model where an interstitial copper (Cu_i), i.e., Cu at a tetrahedral hole that is surrounded by four sulfur atoms, is the blue-emitting center. Wruck *et al.*⁹ suggested that at high temperatures, Cu_i is close to a nearby Cu_Sr , thereby balancing the charge mismatch. They also proposed that Cu_Sr should be optically inactive because of inversion symmetry. However, Cu_Sr is most probably off centered and radiative transition is hence allowed.^{3,20,22,32} Li *et al.*³ suggested that isolated Cu_i is possible because of the small ionic size of the Cu^+ ion. It was noted that the copper ion should experience less ligand field splitting at the tetrahedral than at the octahedral site and, consequently, the lowest excitation state, i.e., the emitting state, may be at higher energy.

Reduced coordination and symmetry lowering are often thought to shift the emission spectrum to longer wavelengths and it is noted here that the symmetry of off-centered Cu_Sr (C_{3v} or C_{2v})^{22,32} is lower than that of tetrahedral Cu_i (T_d). In Li *et al.*'s model,³ charge neutrality is probably balanced by S vacancies. On the other hand, if the S vacancy is a concomitant consequence of Cu^+ doping, then all copper ions may have a V_S nearby and the charge neutrality in the lattice could be achieved by the Sr vacancy, i.e., $2\text{V}_\text{S} + 1\text{V}_\text{Sr}$ for 2 Cu^+ . In that case, there would also be more space in the lattice for the diffusion of copper and other impurities into different lattice positions, thus resulting in different emission colors. Increasing amount of vacancies would reduce symmetry around the copper ion even further, but the symmetry could still be higher at the tetrahedral than at the off-centered octahedral site. On the other hand, it has also been suggested that the charge compensation mechanism can

be long range in nature, and the S vacancy is not necessarily forming a complex with copper.³² In that case, the S vacancies would not change symmetry around the copper.

Electro-optical analyses indicated different electrical behavior for devices emitting different colors. The green-emitting devices transported less charge across the phosphor, were more efficient, and seemed to have less dynamic space charge within the phosphor than the blue-emitting devices. These findings have been also been shown earlier by Keir *et al.*¹⁴ Creation of the dynamic space charge has been ascribed to the impact ionization mechanism.^{33,34} The dynamic space charge makes electron back injection possible, and the back-injected electrons can recombine with the ionized luminescent centers resulting in a TEE²⁴ that has been low in the green-emitting devices in this work. In the studies of SrS:Ce devices, it has been suggested that the probability of electron delocalization, i.e., ionization of Ce, is higher for Ce ions at lower symmetry/distorted sites than at the octahedral sites.^{35,36}

Furthermore, it was proposed that at distorted sites, the excited levels of Ce may locate closer to the bottom of the conduction band, which makes ionization easier.^{35–37} However, in this work, the blue-emitting centers seem to ionize more easily than the green-emitting centers, because the TEE was high in the blue-emitting devices, even though at the blue-emitting sites the symmetry should be higher and distortion smaller than at the green-emitting sites. This gives an opportunity to speculate that the ionization of Cu in the SrS is more efficient at the tetrahedral than in the off-centered octahedral site, assuming that the tetrahedral Cu⁺ is the blue-emitting center. It is also noted that the large ion size of the Ce³⁺ ion probably always confines it to an octahedral site, which may be the reason for the small variation in electrical properties between the different SrS:Ce samples. By contrast, the possibility of Cu⁺ ions locating at different lattice sites may be the reason for the large variation in electrical properties between the different SrS:Cu samples.

In the earlier studies, it was shown that codoping can result in a reduction of the space charge leading to larger phosphor field, and increased efficiency and luminance.^{14,38} On the other hand, this work found that the higher amounts of Cl (Cl_S is a donor) and K (K_{Sr} is an acceptor) seemed to correlate with the blue and green emission, respectively. They may have caused modifications in electron injection and/or transport properties and, thus, also in the dynamic space charge, even though their bulk concentrations were quite low. It has also been suggested that the leading edge emission (LEE) of the SrS:Ce device originates from the impact excitation mechanism.³⁶ The low level of TEE in this work could thus indicate that an impact excitation mechanism is dominant in the green-emitting SrS:Cu devices. However, in the SrS:Cu,Ag study, the LEE was thought to result from the impact ionization mechanism.²⁵ A very detailed electrical characterization would be needed to verify the possible existence of the impact excitation mechanism in the SrS:Cu.

Earlier studies on luminescent sulphide thin-film depositions showed that the use of hydrogen decreased the amount of oxygen, and enhanced the crystallinity and stoichiometry

of the films, thereby increasing the luminance.^{4,11,12} In this study, these types of effects were not seen, but the hydrogen pulsing resulted in green emission. This behavior could mean that hydrogen has enhanced formation of copper pairs, pushed Cu ions into the sites where they emit green light, and/or modified the local environment around Cu in such a way that the emission turned to green. On the other hand, the use of alkali metal coactivators resulted in the green emission in the earlier studies¹⁴ and the presence of potassium seemed to correlate with the green emission also in this study. The green emission was also occasionally obtained in earlier ALD experiments without use of hydrogen. One possible source of potassium in the ALD process can be Sr(thd)₂ which is used as a Sr precursor because its synthesis may result in volatile potassium compounds as impurities. In this study, however, the green emission was obtained only with hydrogen pulsing, which may indicate that hydrogen has enhanced the inclusion of potassium into the films. The role of potassium in the films is not clear, but it may have served as a flux to facilitate the formation of Cu pairs, and/or it may have modified the local environment of Cu in such a way that it emitted the green light.

V. CONCLUSIONS

EL intensity of the SrS:Cu thin films was found to depend on copper concentration and grain size. SIMS results showed that samples with higher chlorine content were blue emitting, whereas the samples with higher potassium content were green emitting. Pulsing of H₂ during the ALD growth of SrS:Cu resulted in green-emitting devices, and it was suggested that hydrogen pulsing enhanced the deposition of potassium into the films, thereby promoting green emission. Different emission colors are thought to result from a different environment around the copper ions and it was suggested that copper pairs and isolated Cu⁺ ions at the off-centered octahedral sites resulted in green emission. Conversely, isolated Cu⁺ ions at the tetrahedral interstitial sites resulted in blue emission. The blue- and green-emitting devices also showed different time-resolved EL behavior, which suggested reduced dynamic space charge within the green-emitting phosphors, leading to higher emission intensity in the green-emitting devices.

Earlier ALD experiments have resulted in green-emitting SrS:Cu devices without the use of hydrogen in the deposition process. One reason for poor reproducibility of blue emission could be the difficulty of controlling the amount and nature of impurities during the synthesis of the metal precursors. These impurities may result in the incorporation of potassium into the SrS:Cu films and thereby producing green emitting devices. Overall, the local environment around copper is difficult to study, which makes any final conclusions concerning the exact reasons for the different emission colors difficult to draw. The emission spectra are usually quite broad, and it is possible that both the blue- and green-emitting centers coexist, with the final emission color depending on the relative amounts of these centers.

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