Blue electroluminescence from multilayered BaS:Eu/Al₂S₃ thin films

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(Received 2 April 2003; accepted 10 October 2003)

Electroluminescent (EL) BaAl₂S₄:Eu devices were prepared with a multilayered phosphor, composed of 10–20 alternating BaS:Eu and Al₂S₃ thin films and a total phosphor thickness of 300 nm. Depending on evaporation and annealing conditions, pure blue EL was obtained (CIE 1931 color coordinates x = 0.120, y = 0.098). The use of this multilayered BaS:Eu/Al₂S₃ structure gave access to additional information on the atomic composition and luminescent properties of europium-doped barium thioaluminates. The composition of the phosphor layer (diffusion properties, oxygen impurities) was characterized using x-ray photoelectron spectroscopy as a function of substrate temperature and annealing parameters. Optical and morphological properties of BaS:Eu and Al₂S₃ thin films are discussed as well. © 2004 American Institute of Physics.

I. INTRODUCTION

In 1999 Miura et al. introduced europium-doped barium thioaluminate (BaAl₂S₄:Eu) as a high-luminance, blue-emitting phosphor for thin-film electroluminescent devices. A specific evaporation technique was used to obtain stoichiometric thin films: namely, pulsed electron beam evaporation using two targets. The electron beam was alternately switched between BaS:Eu and Al₂S₃ targets. The use of a very short duty cycle (10 ms) led to the deposition of far less than a monolayer of BaS:Eu and Al₂S₃ each cycle. In this way stoichiometric BaAl₂S₄:Eu thin films could be obtained, with a blue emission band peaking at 470 nm.

The pulsed electron beam evaporation (pulsed EBE) method with two targets was used by Miura et al. in 1997 for the production of CuGa₂S₄:Ce thin films. Due to the different vapor pressure of the elements of these thiogallates, the preparation of stoichiometric thin films is very difficult with conventional techniques. Similar problems are experienced with thioaluminates: we were unable to produce high quality BaAl₂S₄:Eu thin films when EBE of europium-doped BaAl₂S₄ pellets was tried. The thin films evaporated in this way were hardly transparent and did not show significant electroluminescent emission.

In this paper, we propose an alternative deposition technique, which is very interesting from a fundamental scientific point of view since it enables us to study different aspects of BaAl₂S₄:Eu thin films. The central phosphor layer is composed of alternating BaS:Eu and Al₂S₃ layers, with an individual thickness varying from 15 to 50 nm. Due to the high reactivity of the constituent layers, Ba₅Al₅S₁₀Eu can be formed, and the thin films show bright electroluminescent emission, depending on the BaS/Al₂S₃ ratio. For BaAl₂S₄:Eu, emission at 470 nm can be obtained, typical for these devices. The luminescent, optical, and morphological properties of the devices and the constituent layers will be discussed.

The approach that uses pulsed EBE with two targets can almost be considered as a coevaporation technique, as the electron beam is rapidly switched between the two pellets (with a duty cycle of only 10 ms). The final composition is then determined by the energy fed to the BaS:Eu and Al₂S₃ pellets during the evaporation process. In this way, the link with the properties of BaS:Eu and Al₂S₃ thin films is lost as a mixture of all elements is immediately obtained.

BaAl₂S₄:Eu thin films prepared with pulsed EBE show a high oxygen content, significantly larger than in most other ACTFEL host materials, such as SrS (Ref. 4) and CaS (Ref. 5). In our approach, depending on the evaporation conditions, distinct BaS:Eu and Al₂S₃ layers are present, which will allow us to pinpoint the origin of the oxygen contamination. Furthermore, Eu³⁺ emission is observed in BaS thin films (this work): in the BaAl₂S₄:Eu thin films only Eu²⁺ emission is present. We will present further information on the valence state of europium, which is easily accessible by using the multilayered structure.

Although this multilayered approach yields additional information, the multilayer deposition technique will probably not yield the best thin films (with the highest luminances), when compared to the approach with pulsed EBE using two targets. Indeed, it is perfectly understandable that by using a multilayered approach, one cannot obtain the desired stoichiometry throughout the whole phosphor layer, without the least deviation, even after considerable thermal annealing. This will have a serious impact on the efficient acceleration of the electrons in the BaAl₂S₄:Eu phosphor layer and thus on the obtained luminance. To get a perfect mixture of BaS:Eu and Al₂S₃, one will tend to reduce the individual layer thickness, and in the end the multilayered approach will converge to a pulsed EBE method using two targets.

The peak wavelength of photoluminescent (PL) emission in europium-doped thioaluminate powder is known to be strongly depending on the BaS:Al₂S₃ ratio [BaAl₂S₄ (467

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nm), Ba$_2$Al$_2$S$_5$ (487 nm), Ba$_2$Al$_2$S$_8$ (540 nm)] (Ref. 6) due to the strong influence of the crystal field, as the nearest excited state of Eu$^{2+}$ lies in the outer $d$ shell. Furthermore, the PL of BaAl$_2$S$_4$:Eu shows a higher efficiency and a better thermal quenching behavior than other barium thioaluminates. Miura described the influence of the BaS/Al$_2$S$_3$ ratio on the peak wavelength of the electroluminescent (EL) emission. The emission shifts to longer wavelengths upon an increase in this ratio, in correspondence with the results obtained by Le Thi et al. on powder phosphors.8

II. EXPERIMENT

Sintered BaS:Eu and Al$_2$S$_3$ pellets were used as the source material for electron beam evaporation. BaS (99.9%, CERAC) and EuF$_3$ (99.5%, CERAC) were mixed and pressed into pellets, before sintering in H$_2$S at 800 °C for 1 h. Unless otherwise stated, europium concentration in BaS was 2 mol %. Pressed pellets of Al$_2$S$_3$ (99.9%, CERAC) were sintered as well (H$_2$S, 600 °C, 1 h). To avoid contamination of the source material due to the high reactivity and hygroscopic character of BaS and Al$_2$S$_3$, as many manipulations as possible were performed under a protective nitrogen atmosphere.

Thin films were deposited on ITO-coated Corning 1737 substrates in H$_2$S atmosphere with a partial pressure of 2 × 10$^{-3}$ Pa. As insulating layers, electron beam evaporated Al$_2$O$_3$ (Merck) thin films were used, with an approximate thickness of 300 nm. Here 200-nm-thick ZnS (99.99%, CERAC) thin films were introduced just above and below the emitting layer, acting both as buffering and as electron accelerating layers.

The central phosphor layer consists of an alternating structure of BaS:Eu and Al$_2$S$_3$ layers, with a total thickness of 300 nm. Thicknesses of the different layers are determined from the molar ratio between BaS and Al$_2$S$_3$. Typical evaporation rates are 0.8 nm/s. The idle time between the evaporation of two successive layers is kept short (less than 10 sec) to reduce contamination from residual gasses in the vacuum system.

Ex situ post-deposition annealing was performed in nitrogen [in a rapid thermal anneal (RTA) system (AST Super Heat System 1000)]. Emission spectra were recorded using a microchannel plate intensified optical multichannel analyzer (EG&G OMA III). Optical transmission spectra were obtained using a Cary 500 spectrophotometer. X-ray photoelectron spectroscopic (XPS) measurements were performed with a Perkin Elmer PHI ESCA 5500 system.

III. RESULTS AND DISCUSSION

A. BaS:Eu thin films

Undoped BaS thin films were evaporated on Vycor Corning 7913 substrates at a substrate temperature of 500 °C. The optical transmission spectrum of a 850 nm thin film is shown in Fig. 1(a). Highly transparent thin films were obtained with a refractive index $n = 2.22$ at 500 nm. All peaks in the x-ray diffraction diagram (not shown) could be attributed to BaS, with a preferential [220] orientation. An annealing in H$_2$S (800 °C) pronounced this orientation. The 2θ full width at half maximum decreased upon annealing (from 0.33° to 0.24°), suggesting grain growth. XPS measurements revealed only a slight oxygen contamination in the BaS thin films. We can conclude that nearly stoichiometric thin films can be evaporated at elevated substrate temperature.

Europium ions can generate luminescence in both divalent and trivalent state.7 Eu$^{3+}$ emission originates from forbidden electric–dipole $4f-4f$ ($^5D_0-^7F_J$) transitions, which are hardly affected by the crystal field. Therefore, the emission spectrum is characterized by narrow emission lines. On the other hand, Eu$^{2+}$ emission is based on electric–dipole allowed $5d4f^6-4f^7$ transitions, which leads to a broad emission band. When europium is introduced in a II-VI host as CaS or SrS, divalent broadband emission is usually observed. This emission is largely influenced by the crystal field as the nearest excited state of Eu$^{2+}$ lies in the outer $d$ shell: emission shifts to shorter wavelengths with decreasing crystal field strength. When the host lattice is varied from CaS to SrS to BaS, the luminescence peak in lightly europium-doped powder phosphors shifts from 651 nm to 616 nm to 572 nm.8

The present BaS:Eu thin films show a very weak orange to nearly infrared electroluminescence, depending on the europium concentration (see Fig. 2). BaS:Eu [0.5 mol %] shows a very broad emission band peaking at 740 nm (CIE 1931 color coordinates $x = 0.61, y = 0.33$); the expected broadband emission at 572 nm was not observed. Upon higher driving voltage the Eu$^{3+}$ emission line at 616 nm, corresponding with the $^5D_0-^7F_2$ transition, emerges.

An increase in the europium concentration to 2 mol % leads to higher luminances, and an emission spectrum which is dominated by $4f-4f$ transitions superposed on broadband emission (see Fig. 2). At 5 mol % the emission is solely composed of narrow Eu$^{3+}$ emission bands (CIE 1931 color coordinates $x = 0.66, y = 0.34$). The obtained broadband emission at 572 nm was not observed. Upon higher driving voltage the Eu$^{3+}$ emission line at 616 nm, corresponding with the $^5D_0-^7F_2$ transition, emerges.

The Eu$^{3+}$ emission bands in Fig. 2 are assigned to the $^5D_0-^7F_J$ transitions. If the Eu$^{3+}$ ion occupies a site without
inversion symmetry, the electric–dipole transitions are no longer strictly forbidden and they appear as lines in the spectra. The transitions with $\Delta J = 0, \pm 2$ are hypersensitive to this effect. The $\Delta J = 2$ transition (at 616 nm) is clearly dominating over the other transitions, which indicates that the Eu$^{3+}$ ions occupy lattice positions without inversion symmetry. The elimination of the inversion symmetry in the cubic BaS crystal lattice probably results from the proximity of europium ions (given the rather high dopant concentration).

### B. Al$_2$S$_3$ thin films

Undoped Al$_2$S$_3$ thin films were evaporated on Vycor Corning 7913 substrates at both low (200 °C) and high (500 °C) substrate temperature. Al$_2$S$_3$ thin films are very unstable, as they immediately react with moisture when taken out of the vacuum system. A smell of H$_2$S is detected, suggesting the immediate oxidation of the thin films towards Al$_2$O$_3$. The thin films are initially yellowish-brown, but within minutes after exposure to the ambient atmosphere they become transparent, but slightly scattering. In order to prevent oxidation of the thin film, the absorption edge shifts to shorter wavelengths (below 250 nm).

XRD data showed that Al$_2$S$_3$ thin films evaporated at 200 °C were completely amorphous, as no sharp diffraction peaks were observed in the $10^\circ - 60^\circ$ $2\theta$ range. When evaporated at 500 °C, two small but sharp diffraction peaks (at 30.7° and 31.2° $2\theta$) were visible, which could be assigned to Al$_2$S$_3$. The diffraction angles match diffraction data we obtained from Al$_2$S$_3$ powder and with literature data on Al$_2$S$_3$ powder.

XPS data reveal quite some differences between low- and high-substrate-temperature films. After sputtering of the ZnS capping layer, approximately 40 nm of the Al$_2$S$_3$ thin film was removed prior to XPS measurements. The high reactivity required relatively short measurement times (less than 10 min) to avoid oxidation of the Al$_2$S$_3$ thin films, even in the UHV ambient of the XPS equipment ($10^{-7}$ Pa). The Al $2p$ photoline in XPS consists of two peaks, the larger one at 75.5 eV and the smaller one at 73.2 eV. (Figure 4 shows similar peak shapes in multilayered BaS/Al$_2$S$_3$ devices). Based on this energy difference, the smaller peak could be attributed to metallic Al, while the larger one corresponds to the peak position for Al$_2$O$_3$ or Al$_3$S$_3$, hence aluminum being in a trivalent bound state. Gaussian curves were fitted to determine $I(Al^{3+})/I(Al^{0})$, being the ratio between aluminum in a bound state and aluminum in a metallic state (see Table I).

The oxygen content in thin films evaporated at a substrate temperature of 200 °C is remarkably low. However, the Al:S ratio considerably differs from the desired 2:3 ratio. Taking into account the form of the Al $2p$ photoline, this suggests that part of the thin film is composed of Al instead of Al$_2$S$_3$. At 500 °C, about half of the sulfur is replaced by oxygen, which will have its consequence for the composition of the multilayered devices. At higher substrate temperatures, an increased sulfur deficiency can be expected for sulfide thin films, but apparently outgassing of the vacuum system also leads to increased oxygen incorporation. This can be linked to the XRD results discussed before, which indicated only a weak crystallinity in the thin films. A further optimization of certain evaporation parameters, such as H$_2$S partial pressure and evaporation rate, will probably lead to thin films of higher stoichiometric and crystallographic quality.

As an illustration, the atomic composition of a Al$_2$S$_3$ thin film without protective ZnS layer which was exposed for 24 h to ambient air is given in Table I. The thin film was almost entirely oxidized to Al$_2$O$_3$, as can be expected from the Al:O ratio. Notice also that the XPS peak originating from Al in a metallic state had almost disappeared.

### C. Multilayered BaS:Eu/Al$_2$S$_3$

Besides experimental parameters such as dopant concentration, substrate temperature, growth rate and annealing temperature, etc., several other parameters are introduced when using a multilayered structure. The thickness of the individual layers and their thickness ratio are the most important as they will influence the luminous spectrum and efficiency. This paper does not intend to present an optimization of all these parameters (and thus the achievement of high luminances); it is meant to provide additional information on the structure and optical properties of Ba$_{x}$Al$_{y}$S$_{3}$:Eu that can only be obtained by using this multilayered structure.

<table>
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<th>Capping layer?</th>
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<td>23.9</td>
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<tr>
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<td>1.81</td>
<td>1.56</td>
<td>4.38</td>
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</table>
1. Low substrate temperature

a. XPS results. At relatively low substrate temperature (200 °C), the reactivity of the individual BaS:(Eu) and Al2S3 layers is expected to be limited, which allows us to obtain more or less distinct layers. The upper part of Fig. 3 shows the atomic concentration as a function of sputter time in an as-deposited multilayered structure, with relatively thick constituent layers (30 nm BaS:Eu, 56 nm Al2S3) evaporated at 200 °C. Upper part, as-deposited. Lower part, RTA at 800 °C.

When thinner layers (~30 nm BaS:Eu, ~56 nm Al2S3) evaporated at 200 °C, with thick constituent layers. Al 2p photoline: (a) mixed BaS/Al2S3 region, (b) pure Al2S3 region. Each time, two components were fitted to the Al 2p photoline. Eu 3d5/2 photoline: (c) pure BaS region, (d) mixed BaS/Al2S3 region.

FIG. 4. XPS photolines of Al and Eu in as-deposited multilayered devices evaporated at 200 °C, with thick constituent layers. Al 2p photoline: (a) mixed BaS/Al2S3 region, (b) pure Al2S3 region. Each time, two components were fitted to the Al 2p photoline. Eu 3d5/2 photoline: (c) pure BaS region, (d) mixed BaS/Al2S3 region.

FIG. 3. XPS depth profiles of a multilayered BaS:Eu/Al2S3 device with thick constituent layers (30 nm BaS:Eu, 56 nm Al2S3) evaporated at 200 °C. Upper part, as-deposited. Lower part, RTA at 800 °C.

measurement error typical for XPS. After a rapid thermal anneal process at 800 °C, an almost homogeneous element distribution is obtained (see lower part of Fig. 3). The oxygen concentration is lower than in devices prepared with the two-target pulse-electron-beam evaporation technique by Inoue et al.\textsuperscript{5} In the latter devices (annealed at 920 °C during 2 min) the formation of an Al2O3-rich region was observed between the phosphor layer and the top ZnS buffer layer.\textsuperscript{3,12}

In our devices, the outer thin films of the multilayered phosphor are composed of BaS:Eu, which can be seen in the XPS profile in the as-deposited device (upper part of Fig. 3). After annealing, the interface layer shows an increased Al and O content (Ba:Al ratio ~ 1:3.5), indicating the—premature—formation of an Al2O3 interface layer. The annealing temperature was limited to 800 °C (determined by the annealing point of the Corning substrates), which can explain the absence of an almost pure Al2O3 interface layer. In contrast with the pulsed evaporation technique, which yields an almost continuous evaporation of BaS and Al2S3, the use of a multilayered structure implies sites with higher aluminum and oxygen content (as most of the oxygen contamination originates from the deposition of the Al2S3 thin films), which can locally trigger the formation of Al2O3 precipitates. This can explain the increased Al and O concentration in the region of 14 –17 min sputter time.

Several features are seen in the aluminum and europium photoline shapes. In Al2S3-rich regions, the Al 2p photoline consists of two peaks [see Fig. 4(b)]. The same phenomenon was observed in pure Al2S3 thin films. As discussed above, the peak at higher energy results from aluminum in a bound state (Al2S3 or Al2O3), the other one from metallic Al. In regions where the Al2S3 and BaS layers start to mix up (even with low Ba concentration), the peak at lower energy disappears, indicating a bound state for all Al [see Fig. 4(a)]. This implies that a chemical reaction between the constituent layers takes place during the evaporation process, at least to some extent.

Another feature is the valence state of Eu. In the section on BaS thin films we discussed the emission spectrum of BaS:Eu thin films. The presence of narrow emission lines
indicated a trivalent state for europium. In BaAl$_2$S$_4$:Eu, however, the emission spectrum is characterized solely by a broad emission band. Based on the luminescent spectra of BaS:Eu and BaAl$_2$S$_4$:Eu, we can conclude that a change in the valence state of europium from 3+ to 2+ occurs.

In principle, XPS measurements are an ideal probe to evaluate the valence state of Eu, as the 3$d_{5/2}$ photolines for Eu$^{3+}$ and Eu$^{2+}$ are located at 1136 eV and 1125 eV, respectively. However, the determination by means of XPS measurements is difficult due to the rapid oxidation of Eu$^{2+}$. This effect can be minimized by using only a short measurement time (of the order of 3 min) after each sputter process. The combination of a relatively high europium concentration and a high emission probability of photoelectrons allowed us to obtain sufficiently detailed XPS spectra, even when using such a short measurement time.

In mixed BaS-Al$_2$S$_3$ regions, both photolines from the divalent and trivalent state are present [see Fig. 4(d)]. In pure BaS regions, only photolines from Eu$^{3+}$ are present [see Fig. 4(c)]. Under the same measurement conditions, a clear difference in the europium valence state is observed between BaS:Eu regions and (premature) BaAl$_2$S$_4$:Eu regions. Apparently, the europium valence state changes as soon as Ba, Al, S, and Eu over the XPS-measured thickness of 150 nm. The almost homogeneous distribution of the elements Ba, Al, S, and Eu at 600 °C already shows the blue emission band. Other devices annealed at higher driving voltages.

The substrate temperature plays a critical role in the relation between Ba:Al ratio, outgassing in the vacuum system cannot be neglected, and this leads to higher oxygen incorporation in the phosphor layer.

The use of thicker constituent layers leads to small variations in the Ba:Al ratio when sputtering through the phosphor film. Generally, the S:O ratio follows the Ba:Al ratio, which indicates a better stoichiometry for BaS than for BaS:Eu EL devices, where only emission lines originating from Eu$^{3+}$ emerged. Apparently, the mixing with a small amount of Al$_2$S$_3$ alters the emission characteristics (and the valence state) of europium. In a study of luminescent Ba$_{1-x}$Al$_x$S$_2$:Eu powders, Le Thi et al. found a shift to longer wavelengths when the ratio BaS/Al$_2$S$_3$ increased. For instance, the PL of Ba$_{1-x}$Al$_x$S$_2$:Eu powder peaks at 540 nm.

### 2. High substrate temperature

a. XPS results. At relatively high substrate temperature (550 °C), a strong reactivity between BaS and Al$_2$S$_3$ can be expected. In as-deposited devices composed of thin constituent layers (e.g., thickness of BaS layer: 15 nm), we find an almost homogeneous distribution of the elements Ba, Al, S, O, and Eu over the XPS-measured thickness of 150 nm. The Ba:Al ratio shows little variation, as depicted in Fig. 5(a). The oxygen content is very high; the sulfur concentration hardly reaches 10 at. %.

b. EL emission. Although XPS results indicate a relatively good mixed phosphor layer [see Fig. 5(a)], the limited depth resolution of XPS does not allow us to state that a single BaAl$_2$S$_4$ phase is present in the phosphor layer. Indeed, slight variations in the elemental composition (over the range of a few nanometer) will not be detected by XPS, due to the reasons given in Sec. III C 1a. If the electroluminescent emission is characterized by emission bands other than the desired emission at 470 nm, this indicates that other compounds than BaAl$_2$S$_4$ are present. Generally, two emission bands are observed in the as-deposited devices: one peaking at 470–475 nm and another at 575 nm. Upon higher driving voltage, the former emission band becomes more important. Although the latter one is close to the position where BaS:Eu emission is situated at 600 °C, both samples are formed at 600 °C.

### FIG. 5. Elemental composition of as-deposited multilayered BaS:Eu/Al$_2$S$_3$ devices. (a) Ba:Al ratio in device with thin constituent layers evaporated at 550 °C. (b) Ba:Al ratio and (c) S:O ratio in device with thick constituent layers evaporated at 500 °C.
et al. noticed a similar critical temperature for the PL intensity and spectrum of BaAl$_2$S$_4$:Eu thin films evaporated at different substrate temperatures.

Miura described the influence of the BaS/Al$_2$S$_3$ ratio on the peak wavelength of the EL emission. The emission shifted to longer wavelength upon an increase in this ratio. In our as-deposited devices ($T_{\text{substrate}} = 500–600$ °C), the blue emission band is always peaking at 470 nm, even with deviations of the BaS:Al$_2$S$_3$ ratio from 1:1. This implies BaAl$_2$S$_4$ is preferentially formed over thioaluminates with other BaS:Al$_2$S$_3$ ratio, which can be related to the fact that for the production of barium thioaluminate powders with a ratio other than 1:2:4, temperatures higher than 1000 °C are necessary. Only after annealing (800 °C) is the intended BaS:Al$_2$S$_3$ ratio reflected in the peak wavelength of the EL emission, indicating a further mixture of the elements in the phosphor layer. It is reasonable to assume that the formation temperature of these phases is lower in a thin film environment than in macroscopic powder grains.

In a PL study by Le Thi et al. of europium-doped Ba$_x$Al$_{1-x}$S$_4$ powders, only Ba$_2$Al$_2$S$_5$:Eu showed a favorable thermal quenching behavior near room temperature. This implies that luminescent emission from certain Ba$_x$Al$_{1-x}$S$_4$:Eu thioaluminates might only be visible at lower temperatures. However, even when cooled to 100 K, our as-deposited multilayered devices showed no other strong EL emission bands than the blue one at 470 nm and the orange one, supporting the idea of the preferential formation of Ba$_2$Al$_2$S$_5$:Eu.

After a rapid thermal anneal at 800 °C, only the blue EL emission band remains [see Fig. 6(c), thick constituent layers], and the luminescence increases strongly. The optical transmission of the devices increases as well. Apparently, a further mixing towards a homogeneous distribution occurs.

The luminescence in annealed multilayered devices reaches 15–20 cd/m$^2$ at 1 kHz (sine wave, 30 V above threshold). This is significantly lower than the 180 cd/m$^2$ reported by Miura et al. in 1999 (under similar measurement conditions and dopant concentration) and substantially lower than the reported maximum luminances of 2000 cd/m$^2$ at 1 kHz in improved devices. However, in our devices the driving voltage was limited to approximately 30 V above threshold, due to the limited quality of the Al$_2$O$_3$ insulator layers used in our devices. Annealing at 800 °C largely deteriorated the electrical properties of the insulator, leading to significant leakage currents and poor breakdown characteristics; therefore, no electrical properties (such as $L-V$ characteristics or efficiencies) are presented. In the near future, Ta$_2$O$_5$ or BaTiO$_3$ insulators will be used, as their better thermal resistance and higher dielectric constant, compared to Al$_2$O$_3$, should allow higher performances.

An optimization towards dopant concentration, evaporation, and annealing conditions has not yet been performed. However, it was not the purpose of the present work to obtain higher luminances with the multilayered structure compared to the pulsed EBE method, but rather to focus on the composition, the morphology, etc., of Ba$_2$Al$_2$S$_5$:Eu thin films.

### 3. XRD data

In general, the multilayered thin films show little or no x-ray diffraction peaks originating from the central phosphor layer. The interpretation of the diffraction peaks that are present is complicated by the lack of crystallographic data on barium thioaluminates. Peak positions and intensities have only been calculated for BaAl$_2$S$_4$ and BaAl$_2$S$_5$.

No diffraction peaks besides those stemming from ZnS and Al$_2$O$_3$ are visible in the as-deposited devices with individual layer thicknesses up to 30 nm for BaS (56 nm for Al$_2$S$_3$), up to a substrate temperature of 600 °C.

XPS results (see Sec. III C 1a) indicated that in devices evaporated at low substrate temperature, distinct BaS and Al$_2$S$_3$ layers are present. We noticed already (see Sec. III B) that Al$_2$S$_3$ single layers were almost completely amorphous. Although BaS single layers (see Sec. III A) yield sharp diffraction peaks, in multilayered devices diffraction peaks are absent. This can be explained by a partial reaction of the BaS with the Al$_2$S$_3$ layers and by an inevitable amorphous region at the beginning of each film deposition. It was only in an as-deposited multilayered structure with very thick constituent layers (60 nm for BaS) that rather strong BaS diffraction peaks were observed. Using Scherrer’s formula, a grain size of 25 nm could be derived from the full width at half maximum (FWHM) of the (200) peak. A strong preferential orientation along the (200) plane was observed.

In EL devices annealed at elevated temperatures (800 °C), several small diffraction peaks become visible in the XRD spectra both at low and high substrate temperature. Due to the limited knowledge of the crystallographic properties and the rather complex diffraction pattern (compared to materials such as BaS or ZnS), the interpretation of the diffraction data is difficult and will require further research. Nevertheless, the (311) diffraction peak of BaAl$_2$S$_4$ can be detected in most annealed samples. According to the experiments and the calculations by Inoue et al., this is the peak with the highest diffraction intensity.

The XRD spectra of 370-nm-thick pulsed EBE Ba$_2$Al$_2$S$_4$ devices, shown by Inoue et al., contain only small diffraction peaks, although the devices were annealed at 920 °C.

Tanaka et al. showed, with the use of cross-sectional transmission electron microscopy (TEM), that the Ba$_2$Al$_2$S$_4$ layer...
is almost amorphous and that only in a limited region could 10-nm-wide crystals be detected. The probably less homogeneous elemental distribution in our devices, combined with the lower annealing temperature, can explain the lack of clear diffraction peaks.

4. Influence of ambient during evaporation

As stated before, evaporation at higher substrate temperatures leads to a replacement of sulfur by oxygen. To evaluate the influence of oxygen content in the EL devices, phosphor layers were evaporated in an oxygen ambient, with a partial pressure of $2 \times 10^{-3}$ Pa. XPS measurements showed the atomic ratio (Ba+Eu):Al:O to approach 1:2:4, with only a weak sulphur signal (atomic concentration <4%).

As-deposited layers showed a strong EL emission band at 465 nm and a smaller one at 575 nm. After annealing, only a single emission band peaking at 467 nm remains, which is slightly blueshifted compared to the devices evaporated under $H_2S$ ambient.

Given the very low sulfur signal, it seems unlikely that the EL emission still originates from BaAl$_2$S$_4$:Eu. Nevertheless, these devices show a rather high luminance compared to "standard" devices, up to 15 cd/m$^2$ ($L_{30}$, 1 kHz). Several data can be found on BaAl$_2$O$_4$:Eu powder phosphors, but the emission spectrum seems to be highly dependent on the preparation technique, as emission bands at 410–530 nm are observed.\textsuperscript{15–17} Only limited information is available on BaAl$_2$O$_4$:Eu thin films. Lou et al. reported a cathodoluminescent emission band at 452 nm in BaAl$_2$O$_4$:Eu thin films deposited with a spray pyrolysis method.\textsuperscript{18} Therefore it is difficult to judge on the basis of the emission spectrum whether the observed emission of the EL devices is due to BaAl$_2$O$_4$:Eu or BaAl$_2$S$_4$:Eu.

Oxygen and sulfur are both group-VI elements. Possibly oxygen can substitute for a certain part of the sulfur in a BaAl$_2$S$_4$ crystal structure, before a separate BaAl$_2$O$_4$ phase is formed. However, Inoue et al. assumed the oxygen in BaAl$_2$S$_4$ thin films, deposited with the pulsed EBE, to be in an amorphous BaAl$_2$O$_4$ form.\textsuperscript{3} Further research on this topic is necessary for a good understanding of the BaAl$_2$S$_4$:Eu system.

IV. CONCLUSIONS

Optical and morphological properties of BaS:Eu and Al$_2$S$_3$ thin films have been discussed. The electroluminescent emission in BaS:Eu is dominated by Eu$^{3+}$ emission. The approach of a multilayered BaS:Eu/Al$_2$S$_3$ structure gave access to additional information on the elemental composition and luminescent properties of europium doped barium thioaluminates. At low substrate temperatures, little mixing occurs between the constituent BaS:Eu and Al$_2$S$_3$ layers. The valence state of aluminum and europium in different regions is discussed. Elevated substrate temperatures lead to (1) a considerable mixing of the constituent layers in as-deposited devices, (2) an increase in oxygen concentration, and (3) EL emission bands at 470 nm and 575 nm. Annealing at 800 °C is sufficient to obtain pure blue EL emission.

ACKNOWLEDGMENTS

The authors wish to thank O. Janssens for XRD measurements and U. Demeter for extensive XPS measurements. One of the authors (P.F.S.) is a research assistant of the Fund for Scientific Research–Flanders (Belgium) (FWO-Vlaanderen).

2 N. Miura, in Proceedings of the 21st International Display Research Conference in conjunction with the 8th International Display Workshops (Asia Display/IDW '01), Nagoya, Japan, 2001, p. 1059.