An X-ray photoelectron spectroscopy study of BaAl\textsubscript{2}S\textsubscript{4} thin films

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Abstract

Depth profiling with X-ray photoelectron spectroscopy (XPS) was used to study BaAl\textsubscript{2}S\textsubscript{4}:Eu thin films, which were prepared as a multilayered stack of electron beam deposited BaS:Eu and Al\textsubscript{2}S\textsubscript{3} thin films. A post-deposition thermal annealing at 900 °C was performed to obtain full reaction towards BaAl\textsubscript{2}S\textsubscript{4}:Eu. Depth profiles were recorded for both as-deposited and annealed thin films. The influence of exposure to ambient air prior to and after ex situ annealing on the composition of the films is discussed. XPS photoline positions and shapes are interpreted to understand the formation and degradation of BaAl\textsubscript{2}S\textsubscript{4}:Eu. Such information is highly important for the optimisation of BaAl\textsubscript{2}S\textsubscript{4}:Eu thin films as the blue emitter in inorganic thin film electroluminescent displays.

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1. Introduction

The introduction by Miura et al. of BaAl\textsubscript{2}S\textsubscript{4}:Eu as an efficient inorganic blue phosphor for thin film electroluminescence (EL) can be considered as a breakthrough in the commercial development of inorganic EL as a flat panel display technique [1]. Direct electron-beam deposition of BaAl\textsubscript{2}S\textsubscript{4} source material is not possible due to decomposition of the powder [2], which leads to strong deviations from the intended stoichiometry in the thin films. This problem was successfully overcome in 1999, by using a ‘dual source pulsed e-beam evaporation’, rapidly switching between a BaS:Eu and an Al\textsubscript{2}S\textsubscript{3} powder source [1]. Unfortunately, this approach is not possible in our experimental setup. However, due to the high reactivity of Al\textsubscript{2}S\textsubscript{3} and BaS, we were able to obtain bright, blue electroluminescence with a multi-layered thin film structure [3]. A stack of alternating BaS:Eu and Al\textsubscript{2}S\textsubscript{3} thin films is deposited and a subsequent thermal annealing leads to the formation of BaAl\textsubscript{2}S\textsubscript{4}:Eu. Furthermore, this deposition technique is interesting scientifically, since it enables us to study different aspects of BaAl\textsubscript{2}S\textsubscript{4}:Eu thin films.

Although this phosphor material is attracting a lot of attention from a technological point of view, the available information on the exact composition of the thin films is very scarce. Despite their high luminance, BaAl\textsubscript{2}S\textsubscript{4}:Eu thin films contain a large amount of oxygen when compared to other materials for inorganic electroluminescence (such as CaS and SrS). Inoue and co-workers reported up to 20 at. % of oxygen in the bulk of 920 °C-annealed BaAl\textsubscript{2}S\textsubscript{4}:Eu thin films, with even higher oxygen concentrations at the interfaces, resulting in the formation of Al\textsubscript{2}O\textsubscript{3} [4, 5]. These thin films were deposited at a substrate temperature of 150 °C.

This large oxygen content is related to the limited stability of BaAl\textsubscript{2}S\textsubscript{4}:Eu powder and thin films. We observed a rapid degradation, with strong decrease of the photoluminescence intensity in unprotected, annealed BaAl\textsubscript{2}S\textsubscript{4}:Eu thin films. Reaction with moisture leads to the hydrolysis of the thin films and the evolution of H\textsubscript{2}S gas is observed. For display purposes, BaAl\textsubscript{2}S\textsubscript{4}:Eu thin films are encapsulated by buffer and insulator layers. For long-term stability, however, it is crucial to obtain more information on the formation and degradation...
processes that occur during the different stages of the thin film preparation.

In this work, we show the results of an extensive X-ray photoelectron spectroscopy (XPS) study on as-deposited and annealed BaAl₂S₄:Eu thin films. The influence of ZnS buffer layers (above and below the multi-layer) on the composition and the stability against moisture is also investigated.

2. Experimental

BaS (Alfa, 99.7%) and Al₂S₃ (CERAC, 99.9%) powders were sintered under H₂S for 1 h, at 800 and 600 °C, respectively. After sintering, the powders were sufficiently densified to allow evaporation without the need to press them into pellets.

BaS powder was doped with EuF₃ (CERAC, 99.9%) prior to sintering, with a molar concentration of 1%. Europium was added to check if the photoluminescent behaviour of the thin films was in correspondence with our previous experiments. Since recording high quality XPS spectra of Eu would require a significant amount of time due to the low Eu content in the thin films, this element was not followed during the depth profiles. We treated some aspects of the valence state of europium in previous publications [3,6].

The multi-layers were composed of nine alternatingly deposited BaS:Eu and Al₂S₃ thin films. BaS:Eu was chosen as material for both outer layers, because of its higher stability towards moisture compared to Al₂S₃. Individual layer thicknesses were scaled to obtain an overall 1:1 molar ratio. The BaS:Eu/Al₂S₃ multi-layers were deposited at a substrate temperature of 400 °C and with an H₂S partial pressure of 2 × 10⁻² Pa. 250 to 300 nm thick multi-layers were deposited on corning vycor 7913 substrates, with a deposition rate of about 1 nm/s. Optional ZnS buffer layers were deposited with electron-beam evaporation as well. Compositional information from XPS depth profiling needs to be evaluated with care. Several effects can change the apparent composition, such as preferential sputtering of certain elements, knock-on sputtering and different sputter rates (for instance, in unmixed multi-layered thin films) [7]. Due to the low electric conductivity of the layers, some charging occurred during the XPS measurements. A low energy electron flood gun was used as a neutraliser. However, as perfect neutralisation could not always be guaranteed, absolute peak positions should be interpreted with caution.

Special precautions were taken to limit possible contamination of the starting powders and the thin films due to contact with (inevitably moist) ambient air. Especially, Al₂S₃ is extremely sensitive to moisture, which can be appreciated by the development of a strong H₂S smell. Weighing, transport to the sintering equipment and recuperation of the sintered material were performed under a protective nitrogen atmosphere. Only during the loading of the deposition system, a short contact with ambient air was inevitable. Outgassing in the vacuum chamber due to the substrate heating could be limited to 2 × 10⁻³ Pa. After deposition, thin films were exposed to ambient air for no longer than a few minutes, which was needed to allow for the ex situ thermal annealing and loading into the XPS equipment.

3. Results and discussion

3.1. As-deposited thin film, immediate measurement

Fig. 1 shows the typical depth profile for an as-deposited multi-layered thin film with ZnS buffer layers. It is readily observed that only limited reaction between the individual BaS:Eu and Al₂S₃ thin films has occurred yet. The average oxygen concentration in the phosphor layer is less than 2 at.%, which is much lower than we reported earlier [3], thanks to the precautions taken to limit all contaminations (see Section 2). It is thus possible to deposit a BaS/Al₂S₃ multi-layered thin film with low initial oxygen contamination, even at a relatively high substrate temperature of 400 °C. When an uncontrolled, but temporal increase in base pressure occurred in the vacuum system during deposition, a higher oxygen concentration could be observed in the depth profile, limited to the corresponding region. However, we were able to deposit BaS/Al₂S₃ multi-layered thin films with oxygen concentration below 2 at.% in a reproducible way. The overall Ba:Al:(S + O) ratio differs strongly from 1:2:4, which is
caused by the sulfur deficiency of the Al$_2$S$_3$ layers, as can be readily observed in the Al-rich regions in Fig. 1.

The specific shape of the Al 2p photoline indicates that some kind of reaction has already occurred at the BaS/Al$_2$S$_3$ interfaces. Fig. 2 shows the Al 2p photoline at selected points in the depth profile (Fig. 1). Two Gaussian functions were fitted to the photolines, at varying energy position to correct for possible charging effects of the sample. A good fit for all spectra could be obtained with a constant energy separation of 2.2 eV. In Al$_2$S$_3$-rich regions, which tend to be sulfur deficient (Fig. 1), two almost equal components are observed.

In a previous publication [3], we observed a similar phenomenon in both Al$_2$S$_3$ and BaS/Al$_2$S$_3$ multi-layered thin films. We then attributed the component at higher binding energy to aluminium in a bound state (i.e. Al$_2$S$_3$ or Al$_2$O$_3$), the component at lower energy was related to unbound aluminium. Away from the ‘pure’ Al$_2$S$_3$ regions, more Al is in a bound state. This effect is observed more clearly if BaS is deposited onto a freshly deposited Al$_2$S$_3$ thin film (cycle nos. 30–27 in Fig. 2). Even at low Ba concentrations, the component at higher binding energy becomes more important and close to the ‘pure’ BaS regions, almost all Al is in a bound state. As soon as Al$_2$S$_3$ is deposited onto BaS (cycle nos. 25–22 in Fig. 2), the component at lower binding energy reappears. Throughout this entire region, the photoline shape is rather similar to the one of ‘pure’ Al$_2$S$_3$. This indicates that a better reaction between the constituent layers is obtained when BaS is evaporated onto Al$_2$S$_3$, than vice versa. This is confirmed by the slightly asymmetrical depth profile in Fig. 1. The transition depth between BaS- and Al$_2$S$_3$-rich regions is larger for BaS deposited on top of Al$_2$S$_3$ thin films. Al$_2$S$_3$ regions are considerably more sulfur deficient than BaS, which leaves more Al in an unbound state, ready to react with the BaS being deposited on top of it.

3.2. Immediately annealed thin film, immediate measurement

Depth profiling of a multi-layer (with ZnS buffer layers) after annealing at 900 °C revealed a very homogeneous composition of the bulk of the phosphor layer (Fig. 3). The depth profile is very smooth when compared to earlier results on annealing at 800 °C [2]. The oxygen content has increased to about 7.5 at. % in the bulk and 11 at. % very close to the ZnS/BaAl$_2$S$_4$:Eu interface. As the amount of sulfur remains roughly the same, the increase in oxygen content makes the thin films move towards stoichiometry, if one takes 1:2:4 as the ratio for Ba:Al:(S + O).

Together with the increase in oxygen concentration, a slightly higher Al/Ba ratio is detected at the interface as well. This effect has also been observed in BaAl$_2$S$_4$:Eu thin films deposited with a dual source pulsed e-beam evaporation [4,5]. In that case, the formation of an Al$_2$O$_3$ layer at the interface was much more pronounced however.

Omission of the ZnS buffer layers leads to a strong increase in oxygen concentration at both interfaces. Although bulk oxygen concentration is still around 7 at. %, the interfaces contain up to 20 at. % of oxygen, mainly substituting for sulfur as the Ba:Al:(S + O) ratio is close to the ratio in the bulk of the thin film. The oxygen-rich regions extend deeper into the phosphor layer as well. The situation at the top interface can easily be interpreted as the hydrolysis and oxidation of the multi-layer during the – although very short – exposure to ambient air between recovery of the sample from the deposition system and the ex situ thermal annealing. This effect, accompanied by the development of a H$_2$S smell, has been
confirmed by XPS compositional analysis. The presence of a ZnS buffer layer slows this process and limits the sulfur loss in the thin film. The situation at the bottom interface is more difficult to explain. No obvious source of oxygen is present, apart from the substrate.

The Si 2p photoline shape indeed suggests a (partial) reaction between the substrate and the BaS/Al\(_2\)S\(_3\) multi-layer (Fig. 4). An additional peak is present, shifted over 3.8–4.0 eV to lower binding energy. This corresponds very well [8,9] to the energy difference between Si being in a SiO\(_2\) lattice (high energy peak) and Si being in a Si environment, with possibly additional contributions from Si in an oxygen deficient SiO\(_x\) environment. In both cases, this points at the substrate being a source of oxygen. The low energy peak is only visible at the bottom interface of immediately annealed thin films without ZnS buffer layers.

3.3. Immediately annealed thin film, after exposure to ambient air

Fig. 5 shows the typical depth profile of an annealed multi-layered thin film with ZnS buffer layers, which had been exposed to ambient air for 48 h between annealing and the XPS measurements.

The depth profile is very similar to an immediately measured, annealed multi-layer (Fig. 3), apart from the fact that almost all sulfur in the phosphor layer is substituted by oxygen after exposure to ambient air. The Ba:Al:O ratio is very close to 1:2:4; further research will be necessary to determine whether the main reaction product is actually BaAl\(_2\)O\(_4\).

4. Conclusions and perspectives

By taking special precautions to prevent degradation by contact with moist air, it is possible to obtain BaS:Eu/Al\(_2\)S\(_3\) multi-layered structures with low oxygen content at
elevated substrate temperature. Details on the inter-layer reactions can be derived from the shape of the Al 2p photo-line. The as-deposited thin films are sulfur deficient, however, and upon annealing the oxygen content increases towards a 1:2:4 ratio for Ba$_2$Al$_2$(S+O). ZnS buffer layers are necessary to limit the degradation effect due to contact with moist air. They also eliminate chemical reaction with the bottom interface. Exposure to ambient air leads to a large replacement of sulfur by oxygen. The remaining sulfur resides partially under the form of sulfates.

Future work will include the study of the relation of these compositional observations with the optical and (photo)luminescent properties of BaAl$_2$S$_4$:Eu thin films. Post-deposition annealing in sulfur-rich ambient might be necessary to remediate the sulfur deficiency in the as-deposited films.

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