Sm$^{2+}$-doped SiAlO sputter deposited coatings for self-absorption and scatter-free luminescent solar concentrator applications

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A B S T R A C T

Combinatorial reactive co-sputtering using Al, Si and Sm targets in an Ar + O$_2$ atmosphere, resulted in Sm doped SiAlO thin films with a wide Sm concentration- and Si:Al composition gradient. By combining position dependent EDX spectra and laser excited emission spectra, ternary phase diagrams were constructed that directly show the relation between Sm emission intensity, index of refraction, thickness and composition. Using this approach, the Sm$^{2+}$ and Sm$^{3+}$ emission intensity ratio was controlled towards films with predominantly Sm$^{2+}$ emission, which is most favorable for luminescent solar concentrator (LSC) applications. The optimum Sm$^{2+}$ efficiency was reached when the Al content was about equal to the Sm content. When the Si:Al ratio decreases, the Sm$^{2+}$ emission intensity strongly drops to almost zero. However, sputtering without Al resulted in no Sm$^{2+}$ emission intensity at all. The excitation and emission properties of Sm$^{2+}$ in the optimized thin films, especially the ratio between the 4f→4f and 5d→4f emission that is sensitively susceptible to the co-ordination polyhedron, closely resembles that of Sm$^{2+}$ doped crystalline powders with the same composition. This strongly suggest that the Sm$^{2+}$ ions in our amorphous films are coordinated in the same way. A homogeneous thin film on float glass clearly shows the light concentration effect of the red Sm$^{2+}$ emission. Due to an unexplained low Sm$^{2+}$ absorption of our films, even the optimized thin films do not luminesce brightly.

1. Introduction

Luminescent Solar Concentrators (LSCs) have the potential to play a major role in the transition to net zero-energy buildings (NZEBs) when applied as an electricity generating window [1,2]. A promising design for an LSC is a thin film doped with luminescent centers sputter coated on glass. The thin film absorbs part of the solar spectrum and emits this for an LSC is a thin film doped with luminescent centers sputter coated on glass, this emitted light is concentrated on the edges of the glass. Here, photovoltaic cells convert this concentrated light in electricity. To make the solar concentration process efficient, the thin film should have a strong absorption preferably in the visible spectrum, where 43% of the solar energy is found. Furthermore, the luminescent thin film should have no self-absorption of luminescence [3] and a high quantum yield. As shown by Boer et al. [4], the rare-earth ion samarium (Sm) meets these conditions when doped in the inorganic phosphor SrB$_2$O$_7$. Unfortunately, it appeared difficult to integrate the phosphor particles in a waveguide that does not scatter light, preventing further progress. In this work we take the next step by incorporating Sm in an industry compatible, sputtered SiAlO coating on glass.

Various types of scatter-free, silicon-aluminum-oxygen-nitrogen (SiAlON) coatings are widely used in the glass industry as dielectric window coatings, e.g. for anti-reflection and scratch protection. Previ-ously we have shown that these coatings can be further functionalized by doping with Eu$^{2+}$ luminescence centers [5]. While the 5d-states of Eu$^{2+}$ have a limited absorption spectral range and suffer from self-absorption, the Sm$^{2+}$ 5d-states have a wider absorption range up to 600 nm in the visible spectrum and the 4f→4f Sm$^{2+}$ emission is not self-absorbed by the 5d-states. However, when Sm is doped into the SiAlON sputtered coatings, it occurs not only in the desired divalent (Sm$^{2+}$) valence state but also in the trivalent (Sm$^{3+}$) state which has its main absorption limited to a narrow UV part of the solar spectrum.

In this research we first report how the thin film composition influences the valence state of the Sm ion using a single deposition of a thin film with a Si:Al composition and Sm concentration gradient. This gradient film was deposited by reactive radiofrequency (RF) magnetron co-sputtering on a non-rotating substrate with three different targets under an angle [6]. Subsequently, position dependent electron
dispersive X-ray spectroscopy (EDX), transmission and laser excited emission spectra were recorded to determine the relation between the composition of the film and the Sm\textsuperscript{2+} and Sm\textsuperscript{3+} luminescent intensities as well as film thickness and refractive index. We will show that the Sm\textsuperscript{2+}/Sm\textsuperscript{3+} emission intensity ratio can be controlled by tuning the Si:Al ratio. Next we use this control to deposit a second gradient film with lower Al-content with almost exclusively Sm\textsuperscript{3+} emission. Finally, we present a homogeneous film with an optimized Si:Al ratio to qualitatively demonstrate the Sm\textsuperscript{3+} LSC effect in a film on 100 × 100 × 6 mm\textsuperscript{3} glass substrate.

2. Methods

2.1. Sample creation

Two SiAlO:Sm thin films were deposited by an AJA ATC Orion 8 magnetron sputtering system with a base pressure of 1 × 10\textsuperscript{−7} Torr (1.3 × 10\textsuperscript{−10} bar) at room temperature (Fig. 1a). After the targets were installed, the walls of the sputter-chamber were heated to 110 °C for 10 h to remove any remaining vapor. Before deposition, the chamber was DC sputtered with a 2-inch metallic Ti (99.2%–99.7%, Lesker) target for 1 h at 20 W to reduce contamination and water vapor, and as an adhesion layer for other sputtered materials during sputtering, so that they do not flake off the chamber walls.

The thin films were deposited on 50 × 50 × 1 mm\textsuperscript{3} square UV grade double-sided polished MgF\textsubscript{2} substrates (Roditi). MgF\textsubscript{2} was chosen as substrate, because glass-type substrates consist of SiO\textsubscript{2} which could lead to misinterpretation of EDX measurements. The substrate was sequentially rinsed three times with ethanol (96%) and demineralized water. The sputtering was done by three metallic Si (99.9999%, Lesker), Al (99.99995%, Lesker) and Sm (99.9%, Demaco) targets, all 5 cm in diameter. These targets were oriented such that the reactively co-sputtered material would reach the substrates from three different sides, as shown in Fig. 1a. On the Sm source a stainless steel mask with a pattern of concentric holes was put covering 85% of the Sm target to reduce the Sm deposition rate. The depositions took place at room temperature and at a working pressure of 3 mTorr (4 × 10\textsuperscript{−6} bar), sustained by gas flows of 18 sccm 5 N purity Ar, introduced at the Al source, and of 1.2 sccm 5 N purity O\textsubscript{2}, introduced next to the substrate. For the first sample, the guns of Si, Al and Sm operated at powers of 60 W RF, 60 W DC, and 25 W RF respectively for a total duration of 11.25 h. No heat treatment was used during or after deposition of the thin film. The second sample had gun powers of 120 W RF, 20 W DC an 25 W RF on the Si, Al and Sm guns respectively. In this case two masks were used, covering 85% and 60% of the Sm and the Al target, respectively.

![Fig. 1. Fabrication of the compositional library of a SiAlO:Sm sample with gradients of Si, Al and Sm. (a) Photograph of the sputter set-up showing the four guns. A mask is placed on top of the Sm gun. The Ti gun is not used for fabrication of the samples. (b) Photograph of the first sample. The thin film is transparent and under this angle the interference fringes can be seen. The Si, Sm and Al-rich sides are on the left, top and right respectively.](image)

2.2. Emission spectra

For the emission spectra, the samples were excited by a wavelength tunable EKSPLA NT230 OPO laser. A grid of 32 × 32 different emission spectra across the sample was measured by using two Thorlabs DDSM100 linear translation stages stacked perpendicularly on top of each other. Longpass filters of 300 nm and 405 nm were used to eliminate the reflected laser light of 240 nm and 360 nm used to excite the sample. A 600 μm diameter multimode optical fiber directed the emitted light to a spectrometer (Ocean Optics QE65000), measuring the photoluminescence with integration times of 1000 ms, averaged 3 times. The emission intensities were corrected for the wavelength dependent efficiency and non-linearity of the spectrometer. For further details on the set-up and technique, we refer to Ref. [5].

2.3. Transmission spectra

A Xenon lamp (Hamamatsu, C7535) was used to measure the total transmission through the sample. The light from the Xe lamp is guided through a fiber and collimated (2.7 mm spot diameter) at the sample surface. The light transmitted through the sample is captured by a 5.08 cm diameter integrating sphere (IS200-4, Thorlabs), with an Ocean Optics QEPro spectrometer (200 μm slit width) connected with a multimode optical fiber to the off-axis detector port. The same translation stages used for the emission spectra were used to measure a grid of 24 × 24 transmission spectra across the substrate. The spectra were corrected for the baseline (when no light enters the integrating sphere) and divided by the spectrum measured when the integrating sphere was exposed to direct light from the Xe lamp. The transmission spectra were measured with an integration time of 300 ms and were averaged 20 times.

2.4. EDX

Energy-dispersive X-ray spectroscopy (EDX) measurements were done on 39 coordinates on the first sample and 23 coordinates on the second sample to determine the local concentrations of the chemical elements. A JEOL IT-100 EDX/SEM, operating at a voltage of 15 kV with a probe current at 70% and low vacuum mode of 35 Pa pressure provides the possibility of analysis without having to add a conductive layer to the thin film. The sample was attached to the holder with carbon tape and the measurements were performed in Backscattered Electron Shadow (BES) mode. The measurement was conducted at 1000 × magnification.

2.5. XRD

To show the amorphous nature of the thin films, X-ray Diffraction (XRD) measurements were performed. A PANalytical X’pert Pro MPD diffractometer with a Cu Kα anode (λ = 0.1540598 nm) operating at 45 kV and 40 mA for 11 and 1 h was used for the first and second sample respectively. The area illuminated by the X-ray beam was around 1 × 5 mm\textsuperscript{2} in size and was measured in the middle of the samples. All of our thin films appeared to be amorphous. An example XRD spectrum is shown in the supplementary information section.

2.6. Quantum efficiency

The external quantum efficiency defined as the ratio of emitted photons to the absorbed photons by the LSC sample was measured according to the method described in Refs. [7]. As an excitation source, an EKSPLA NT230 OPO laser set to 360 nm was coupled in a 5.3 inch Labsphere integrating sphere. The resulting spectra were measured at on-off-axis detector port with an Ocean Optics QEPro spectrometer with an integration time of 400 ms and averaged over 80 scans.
To realize a SiAlO:Sm thin film, the substrate was sputtered from three different sides by Si, Sm and Al sputter guns. By not rotating the sample during deposition, a concentration gradient of the three elements was established. Fig. 1a shows the sputter gun configuration. The substrate is located above the guns. The Ti target is not used for fabricating of the sample but rather to improve the vacuum of the sputter chamber.

Fig. 1b shows the as-deposited thin film where Si is sputtered from the left side (x = 0 mm), Sm is sputtered from the top side (y = 0 mm), and Al is sputtered from the right side (x = 50 mm). In all following figures, the orientation of Fig. 1b will be used. The sputtered SiAlO:Sm thin film is transparent and shows interference fringes that arise due to the difference in refractive index of the film and the substrate and due to the thickness gradient. Because the Al gun settings resulted in a higher sputtering yield than the Si gun, the interference fringes follow the Al sputtering direction. The roundness of the fringes originate from the radial sputter distribution of the targets.

Using an xy-scanning set-up [6], transmission measurements were performed on 24 × 24 distinct coordinates on the sample. Each transmission spectrum was fitted with a model as explained in Ref. [5,6]. This model yields the thickness and refractive index of the film as a function of position. Fig. 2a shows the film thickness in μm, which ranges from 2.8 μm on the Si-rich side to 4.8 μm on the Al-rich side. The thickness is zero in the bottom-left and top-right because no coating is applied here due to the clips that fixed the substrate in place.

To determine the local concentrations of the Si, Al and Sm cations, EDX measurements were performed on 39 coordinates of the thin film. The white dots in Fig. 3a indicate the 39 locations where EDX measurements were performed. The surface-source equation [5,10] was used to interpolate between the 39 coordinates to get a continuous distribution. Fig. 3a, b and c show the Si, Sm and Al cation concentration respectively. Since Si was sputtered from the left, Sm from the top and Al from the right, as expected, the highest Si concentration is found on the left, the highest Sm concentration in the top-left, and the highest Al concentration is found on the right. To obtain a higher Al concentration compared to Si, Al was DC sputtered and Sm was RF sputtered. The difference in sputtering yields of Al and Si also results in the shape of the Sm gradient. Fig. 3d, e and f show the Si, Sm and Al cation concentration respectively of a sample that will be discussed later. The areas in Fig. 3g show the range of cation concentrations in % in a ternary diagram. The blue area in the bottom right corner describes the concentration range of this sample, the red area in the bottom left describes a range of the sample which will be discussed later. In this sample, Si ranges from 4.0 to 37.5 at.%, Sm ranges from 1.6 to 9.5 at.%, and Al ranges from 56.0 to 94.4 at.%. Note that by using a larger substrate or by depositing multiple films the entire ternary diagram can be filled.

Emission spectra were recorded at 32×32 distinct coordinates across the substrate at an excitation wavelength of 360 nm, mostly exciting Sm3+ ions in their 5d-state. Gaussian distributions were fitted to all 32 × 32 emission spectra, of which one example is shown in Fig. 4a. Fig. 4b and c show emission spectra at some of these locations. The sharp emission peaks as shown in Fig. 4a at wavelengths of 682 nm, 700 nm, 725 nm, 761 nm, and 809 nm are assigned to the $^{5}D_{0} \rightarrow ^{7}F_{0}$, $^{5}D_{0} \rightarrow ^{7}F_{1}$, $^{5}D_{0} \rightarrow ^{7}F_{2}$, $^{5}D_{0} \rightarrow ^{7}F_{3}$, and $^{5}D_{0} \rightarrow ^{7}F_{4}$ of Sm3+ [11] respectively. The $^{5}D_{0} \rightarrow ^{7}F_{0}$ transition is the only nondegenerate 4f→4f transition. Hence, it is the sharpest. Next to the peaks associated with Sm3+, peaks with lower intensity related to 4f→4f transitions in Sm2+ at 599 nm and 646 nm are observed. These peaks are assigned to the $^{5}G_{5/2} \rightarrow ^{7}H_{2}$ and $^{5}G_{7/2} \rightarrow ^{7}H_{0}$ transitions respectively. Furthermore, two broad bands between 600 and 900 nm can be observed which we tentatively assign to Sm2+ 4f5d→4f emission.

By correlating the concentrations of Fig. 3 to the position dependent $^{5}D_{0} \rightarrow ^{7}F_{2}$ emission intensity of the fitted peaks, the emission intensities could be directly related to the local compositions. Fig. 4d shows the result of this correlation in a zoomed-in ternary diagram. The emission is most intense in the area where the Si concentration is highest, the Al concentration is lowest, and the Sm concentration is lowest.

Fig. 4d includes 3 so-called Sm iso-lines with a constant Sm concentration but changing Al:Si ratio and 3 Al:Si iso-lines where the Sm concentration varies. The 4f→4f line emission intensity appears to decrease with increasing Sm concentrations for all Al:Si ratios. We assign this drop in intensity with increasing Sm concentration to a concentration quenching mechanism that has been observed before in Sm2+ doped phosphors [12-14].

The ternary phase diagram also provides the opportunity to study the Sm3+ emission intensity as a function of the Al:Si ratio while keeping the Sm at.% constant. In this case, the intensity needs to be monitored along horizontal lines in the phase-diagram. As can be seen in the inset of Fig. 4b, it follows for example that for a Sm concentration of 5 at.% the emission intensity decreases by a factor of 60 when the Si/(Si + Al) ratio changes from 0.38 to 0.07, showing the strong dependence of emission intensity on local composition. The strongest Sm3+ emission is found in a Si-rich environment where the Sm concentration is the lowest.

The same approach can be repeated at an excitation wavelength of 240 nm at which mostly the Sm3+ charge transfer band is excited. Fig. 5a shows an example of the Gaussian functions that were fitted to the emission peaks at all 32 × 32 locations. In Fig. 5b and c, emission spectra are shown for different locations on the substrate. In contrast to 360 nm excitation, we mainly observe Sm3+ 4f→4f emission. The peaks at wavelengths of 562 nm, 599 nm, 646 nm and 710 nm are assigned to $^{4}G_{5/2} \rightarrow ^{4}H_{5/2}$, $^{4}G_{5/2} \rightarrow ^{4}H_{7/2}$, $^{4}G_{5/2} \rightarrow ^{4}H_{9/2}$ and $^{4}G_{9/2} \rightarrow ^{4}H_{11/2}$ transitions of Sm3+ respectively [11]. Fig. 5d shows a ternary diagram of the integrated intensities of the $^{4}G_{5/2} \rightarrow ^{4}H_{5/2}$ emission peaks directly relating composition to Sm3+ emission intensity.

The ternary diagram of Fig. 5d can be used to study the Sm3+ emission intensity as a function of the Sm concentration for constant Al:Si ratio as well as a function of the Al:Si ratios for constant Sm concentration. The PL intensity increases linearly by a factor of about 2 for constant Al:Si ratio while the Sm concentration decreases from 5.5 to 2.6 at.% (at Al:Si = 90:10, see the inset of Fig. 5e). This increase in emission intensity with increasing concentration is again ascribed to concentration quenching. The Sm3+ emission intensity increases by about a factor of 2 when the Si/(Si + Al) ratio decreases from 0.38 to 0.07 at 5 at.% Sm concentration (see the inset of Fig. 5b). This intensity decrease with Si/(Si + Al) ratio is much smaller compared to the 60 times decrease for Sm3+ emission mentioned earlier. The emission properties of Sm3+ seem to be less sensitive to the local composition.

![Fig. 2. Properties of the thin film library. (a) The position-dependent thickness of the deposited thin film in μm. (b) The position-dependent refractive index of the thin film.](image-url)
compared to Sm\(^{2+}\) emission and is strongest in the Sm-poor and Al-rich portion of the composition range.

The ternary phase diagrams presented in Figs. 4d and 5d predict that a thin film with optimized Sm\(^{2+}\) emission intensity and minimal to no Sm\(^{3+}\) emission can be made by drastically increasing the Si:Al ratio. For this reason a gradient SiAlO:Sm thin film was sputtered with concentrations in the Si-rich corner of the ternary diagram as shown by the red area in the bottom left corner of the ternary diagram in Fig. 3g. A grid of 20 × 20 emission spectra were measured under 360 nm excitation. Fig. 6a shows the excitation and emission spectra measured after the sample had been annealed. Almost exclusively Sm\(^{2+}\) emission is observed and the shapes of the emission spectra are identical to those measured in the first sample. To link the emission intensities to the local concentrations, 23 EDX measurements were performed and interpolated over the substrate by the same method as applied to the first sample (see Fig. 3d). The resulting ternary diagram can be found in Fig. 6b. Si ranges from 68.0 to 92.0 at.%, Sm ranges from 4.7 to 15.4 at.% and Al ranges from 3.3 to 16.6 at.%. The optimized emission intensity is found for a Si:Al ratio of 23:1, or more specifically, for a concentration ratio of 91.5 at.% Si, 4.7 at.% Sm, and 3.9 at.% Al. This result raised the question whether Al is needed at all for an optimal Sm\(^{2+}\) emission. Thus, a sample was sputtered which had identical sputtering settings apart from the fact that no Al was co-sputtered. After exciting this sample at 360 nm, no Sm\(^{2+}\) nor Sm\(^{3+}\) emission could be observed. It is therefore concluded that small amounts of Al are needed for the sample to exhibit Sm\(^{2+}\) emission.

To demonstrate the LSC application, a SiAlO:Sm\(^{2+}\) thin film was sputtered onto a 100 × 100 × 6 mm\(^3\) float glass substrate by utilizing the outcomes of the second sample discussed above. After annealing the substrate, it was put under a UV light source. A photograph shown in...
Fig. 4. Emission spectra of the first sample excited at 360 nm. (a) The deconvolution of a Sm$^{2+}$ emission spectrum. (b) Five emission spectra measured along a Sm-isoline of 5 at.% Sm. An overview of the emission intensities as a function of Si/(Si + Al) ratios for three different Sm at.% are depicted in the inset. (c) Another three emission spectra measured along an Al:Si-isoline of Al:Si = 80:20. In this case the emission intensities as a function of Sm at.% are displayed in the inset for 3 different Al:Si ratios. (d) A ternary diagram directly relates the Sm$^{2+}$ emission intensities to the local concentrations. The numbers on the contour lines indicate relative emission intensities.

Fig. 5. Emission spectra of the first sample excited at 240 nm. (a) The deconvolution of a Sm$^{3+}$ emission spectrum. (b) Five emission spectra measured along a Sm-isoline of 5 at.% Sm. An overview of the emission intensities as a function of Si/(Si + Al) ratios for three different Sm at.% are depicted in the inset. (c) Another three emission spectra measured along an Al:Si-isoline of Al:Si = 70:30. In this case the emission intensities as a function of Sm at.% are displayed in the inset for 3 different Al:Si ratios. (d) A ternary diagram directly relates the Sm$^{3+}$ emission intensities to the local concentrations. The numbers on the contour lines indicate relative emission intensities (scaled to this figure, these numbers should not be used to compare intensities with those reported in Fig. 4).
The Sm$^{2+}$ 4f$^6$→4f$^6$ emission after 4f$^6$→4f$^5$5d excitation at 360 nm is due to an interconfigurational energy transfer from the lowest energy relaxed Sm$^{2+}$ 5d states to the excited Sm$^{3+}$ 4f levels [15]. We observe that when the 4f$^6$→4f$^6$ emission intensity from Sm$^{2+}$ decreases, also the broad emitting bands between 600 and 900 nm also decrease. These broad bands do not show a similar correlation with the f→f transitions coming from Sm$^{3+}$. We therefore ascribe these broad bands to 4f$^5$5d→4f$^6$ emission from Sm$^{2+}$. Furthermore, we observe that these band not only retain the same intensity ratio to the 4f$^6$→4f$^6$ emission lines from Sm$^{3+}$, this 4f$^5$5d→4f$^6$ emission also occurs at the same wavelength, i.e. energy, irrespective of the Si:Al ratio in our sample. Both the efficiency of the 4f$^5$5d→4f$^6$ transition, expressed as intensity, as well as the energy at which this transition occurs are sensitively susceptible to the coordinating polyhedron of Sm$^{2+}$. A small change in coordinating polyhedron would be expressed in a shift in energy of the 4f$^5$5d→4f$^6$ transition, or a shift in its intensity relative to the 4f$^6$→4f$^6$ lines. These observations can be therefore be explained by assuming that Sm$^{2+}$ ions can only emit efficiently in one specific coordinating polyhedron that has a strong tendency to form, irrespective of the composition.

This suggestion is supported by the fact that Sm emission in phosphors, with varying composition and phases like mullite or crystalloballite, again show the same intensity ratio despite the fact that films and powdered phosphors are made in an entirely different way. A comparison of the emission of our films and our powdered phosphors can be found in the Supplementary Information.

As our films are amorphous it is difficult to determine how the Sm ions enter the SiAlO host and deduce the local coordination around Sm in terms of size and symmetry of the Sm site. Our main observations can however be qualitatively understood by a comparison with extensive published work on SiO$_2$ glasses doped with rare earth ions [16] including Sm [14,17–20] in relation with the development of lasers, optical memories or amplifiers.

Our results show that the intensity of the emission changes dramatically as the local composition of our film changes. The intensity of Sm emission in SiO$_2$ glasses is strongly controlled by the poor solubility of Sm and rare earth ions in general, because there is no regular site for Sm in the compact SiO$_2$ amorphous structure with closely condensed SiO$_4$ structural units.

Nogami et al. [14] for example showed that concentration quenching already takes place at a much lower concentration than was expected based on a homogeneous distribution of doping ions, suggesting the tendency of Sm ions to form Sm$_2$O$_3$ or Sm metallic clusters. The same conclusions were drawn for other rare earth ions [21]. Talbot et al. [22] explicitly visualised these clusters by atom probe techniques in Er doped fibres. Our transmission spectra, presented in the supplement section, confirm the poor Sm solubility. The absorption spectra indeed show that we have very low absorption intensity (<1%) despite relatively thick (3–4 μm) and highly doped (2–8 at.%) films. This is very much in contrast to our recent work on Eu$^{2+}$ doped SiAlON thin films, sputtered under similar conditions, where we have reported about 30–50% 4f$^6$→4f$^5$5d absorption in 400–600 nm thick gradient thin films with about 10 at.% of Eu$^{2+}$ doping [5]. Thus we conclude that our films have much lower Sm$^{2+}$ doping % than the Sm content shown in Fig. 2, established by EDX. Our data does not allow us to conclude whether Sm is included as Sm2O3 or metallic clusters instead as suggested in other work mentioned above. This is in line with typical published concentration in SiO$_2$ glasses that are never higher than 1 at.% [14,17,19].
Solubility of Sm can however be enhanced by co-doping with Al. In addition co-doping with Al promotes the Ln\(^{3+}\)→Ln\(^{2+}\) transition in case of Yb and Sm [14,23].

Morimoto et al. [17], inspired by earlier work on Nd\(^{3+}\) by Arai et al. [24] was the first to observe a 10-fold enhancement of Sm\(^{3+}\) fluorescent Intensity in a SiO\(_2\)1%Sm glass by 10% Al co-doping. Their EXAFS study, combined with an assumed concentration quenching of the Sm\(^{3+}\) emission, revealed that at higher Sm concentration, Sm agglomeration in the form of an amorphous Sm oxide phase takes place. In addition it was shown that Al co-doping ions are preferentially coordinating the Sm ions in a local shell. It was therefore concluded that the enhanced fluorescence by Al co-doping was due to a reduction of Sm agglomeration and the corresponding reduction in concentration quenching [17]. Furthermore Jin et al. [19] concluded, based on NMR studies, that the incorporation of Sm into 10Al\(_2\)O\(_3\)–90SiO\(_2\) glass promotes the formation of Al\(_2\)O\(_3\) structural units at the sacrifice of AlO\(_2\) structural units. By comparing NMR data of mullite crystals it was suggested that when Sm\(^{3+}\) or Sm\(^{2+}\) enters the silica structure the extra positive charge is compensated by extra negative charge by replacing SiO\(_2\) units with AlO\(_2\) units. It is suggested that Sm ions enter at similar large oxygen vacancy sites identical to mullite [14,19] because of the large ionic radius of Sm\(^{3+}\) and Sm\(^{2+}\) and related large coordination number. The same conclusion was drawn for other RE ions in SiAlO glasses like Eu\(^{2+}\) [25], Ce\(^{3+}\) [26] and Er\(^{3+}\) [27].

The composition of our Sm\(^{2+}\) films with optimized intensity was 91.5 at.% Si, 4.7 at.% Sm, and 3.9 at.% Al. This is very close to the composition of well-studied amorphous SiO\(_2\) thin glass fibers, co-doped with Sm and Al described above. Hence, it is justified to apply knowledge about the glasses to our films. It is clear from our study that Sm\(^{2+}\) has extremely low solubility in SiO\(_2\) thin films as no luminescence could be observed when no Al ions were co-sputtered. Only with Al co-sputtering, Sm\(^{2+}\) emission could be observed. As can be seen in Fig. 6b, the Sm\(^{2+}\) intensity reaches an optimum at a 3.9 at.% Al due to a enhancement of the solubility of Sm. A further increase of the Al at.% lowers the Sm\(^{2+}\) intensity significantly. Apparently, when the Al concentration increases to much higher values than the Sm\(^{2+}\) concentration, the amorphous host no longer supports the favorable sites for the large Sm\(^{2+}\) ions causing the Sm\(^{2+}\) emission to drop.

Although our film shows luminescence as deposited, the intensity can be enhanced by annealing at 650 °C. Futugami et al. [18] was the first to report on Sm doped thin films made by RF magnetron sputtering of a SiO\(_2\)-Al\(_2\)O\(_3\)-Sm\(_2\)O\(_3\) target sintered at 1490 °C at 16.9 MPa. Their films showed weak Sm\(^{2+}\) and no Sm\(^{3+}\) luminescence as deposited. Sm\(^{2+}\) emission only appeared after heating at 300 °C in air, while the Sm\(^{3+}\) emission remained constant. It was explained by an “optical activation” during which the thermal energy enables the above described local coordination of Sm. Zanatta et al. [15] made SiO\(_2\) thin films by RF sputtering of a Si target with SmO\(_2\) on top. Their sub-oxide SiO\(_2\) films showed the strongest emission after annealing in air at 1000 °C. This was explained by a widening of the SiO\(_2\) bandgap and a drop in the number of non-radiative centers in the bandgap. As our films are almost stoichiometric (SiO\(_2\)), it is likely that film annealing in our case causes a similar optical activation as described in Ref. [18] through a structural rearrangement around the Sm\(^{2+}\) ions, resulting in the earlier described Sm\(^{2+}\) site in the amorphous structure.

Finally, a note on the observed Sm\(^{3+}\) emission. Fig. 4 shows that the optimum Sm\(^{3+}\) intensity under 240 nm excitation is at the highest observed Al concentration in our films of more than 10 at.%. At these high Al concentrations the structure becomes more like Al\(_2\)O\(_3\) as opposed to SiO\(_2\) in which the Sm ion prefers to be in the trivalent state. Similar explanations are given for e.g. Eu in SiO\(_2\) [25,28]. Given the intensity map of the Sm\(^{3+}\) emission presented in Fig. 4 we may conclude that the Sm\(^{3+}\) emission in our films is from Al\(_2\)O\(_3\) related sites in our amorphous films.

4. Conclusions

Scatter-free coating on glass with Sm\(^{2+}\) emission can be made using an industry compatible reactive sputtering method. The Sm\(^{2+}\) 5d-states have a wide excitation range up to 600 nm in the visible spectrum and the 4f\(^{2}\)→4f\(^{4}\) Sm\(^{2+}\) emission is not self-absorbed by the 5d-states due to inter-configurational non-radiative 4f\(^{5}\)d\(^{4}\)→4f\(^{4}\) relaxation. This makes Sm\(^{2+}\) in SiAlO promising candidate materials to realize an electricity generating window based on the LSC principle. From the composition independent constant ratio of 4f\(^{2}\)→4f\(^{4}\) and 4f\(^{5}\)d\(^{4}\)→4f\(^{4}\) emission intensity, we propose that the Sm\(^{2+}\) emission is always from the same Sm\(^{3+}\) site in the SiAlO amorphous structure. Sm valence can be controlled in the desired 2+ state and its intensity optimized by tuning the Si:Al ratio to 23.1. Without any Al co-doping no Sm\(^{2+}\) emission is observed. An unexplained low Sm\(^{2+}\) 4f\(^{5}\)d\(^{4}\)→4f\(^{4}\) absorption is found, despite a Sm doping concentration up to 9% and 4.5 μm thick layers. Based on earlier work, we speculate that metallic Sm or SmO\(_2\) nano-inclusion might cause this low Sm\(^{2+}\) 4f\(^{5}\)d\(^{4}\)→4f\(^{4}\) absorption. Because of the resemblance between our thin-film data and data on Sm\(^{2+}\) doped crystalline phosphors, we suggest that Sm ions enter at the large oxygen vacancy sites identical to that in mullite and SiO\(_2\) glasses.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

David de Vries: Conceptualization, Software, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization.

Sadiq van Overbeek: Conceptualization, Validation, Writing - original draft, Writing - review & editing, Supervision.

Ewert P.J. Merks: Methodology, Software, Validation, Formal analysis, Data curation, Writing - review & editing, Visualization.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jlumin.2020.117321.

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