Intense NIR emission in $\text{YVO}_4:\text{Yb}^{3+}$ thin films by Atomic Layer Deposition

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We demonstrate controlled deposition by atomic layer deposition of $\text{YVO}_4:\text{Yb}^{3+}$ thin films exhibiting an intense NIR emission under UV excitation after post deposition annealing at 1000 °C. The samples are deposited using the precursor combinations $\text{Yb}(\text{thd})_3$, $\text{Y}(\text{thd})_3$ and $\text{VO}(\text{thd})_2$ with O_3 (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) at deposition temperatures between 260–300 °C. The NIR emission is expected to be due to a quantum splitting process in which one UV photon is converted to two NIR photons. In the present contribution we assess the efficiency of the UV to NIR conversion in the produced films and determine the optimal pulse parameters with respect to NIR emission intensity. We also demonstrate synthesis of crystalline $\text{YVO}_4:\text{YbVO}_4$ layered material by ALD to verify the possibility of creating artificial core-shell type structures. The structure, thickness and composition of the deposited films have been studied by X-ray diffraction, ellipsometry, and X-ray fluorescence, respectively.

Introduction

Luminescent materials are attractive for a wide range of applications, like lasers,¹ LEDs,^{2,3} scintillators,^{4,5} sensors^{6,7} and biological markers,^{8,9} and possibly as UV to near-infrared (NIR) converters for increasing the efficiency of solar cells.¹⁰ As solar cells have been identified as a key energy source in the years to come, finding ways to increase their efficiency can have a dramatic impact on the world's energy production.

$\text{YVO}_4:\text{Yb}^{3+}$ has previously been suggested to display down conversion within the energy range of the solar spectrum.^{11–13} Down conversion is a process in which one high energy photon is converted to two or more lower energy photons, consequently allowing for quantum efficiencies of >100%. In $\text{YVO}_4:\text{Yb}^{3+}$ this is accomplished by transferring energy absorbed by $(\text{VO}_4)^{3-}$ via cooperative energy transfer (CET) to two nearby Yb^{3+} ions which emit two NIR photons. YVO_4 is a widely used host material for lanthanides^{14–19} due to the asymmetric environment of the Ln^{3+} position, partially relaxing the Laporte rule, and allowing for high spontaneous emission rates, despite the f-f transitions in lanthanides being parity forbidden. Yb^{3+} emits photons in the range of 980–1050 nm, which is ideal with respect to the band gap of silicon, corresponding to photons with a wavelength of 1100 nm. As YVO_4 is transparent in the 400–1100 nm range^{20,21} it will only absorb energy not well utilized by silicon. The strong charge transfer absorption of the $(\text{VO}_4)^{3-}$ complex allows for application of rather thin layers as efficient UV absorbent, rendering YVO_4 to be a highly suitable host material for integration into silicon based photovoltaics.

$\text{YVO}_4:\text{Eu}^{3+}$ has already been established as a material able to

reduce UV degradation of TiO_2 based organometal halide perovskite based solar cells, while simultaneously increasing light harvesting capabilities.¹⁷ In a study by Cheng *et al.*,¹² it was determined that a sample with 1 mol% Yb^{3+} should have a theoretical upper-limit quantum efficiency of 148.7%, while ignoring concentration quenching and setting the quantum efficiency of $(\text{VO}_4)^{3-}$ and Yb^{3+} to 100%. If it would be possible to reach anywhere near this theoretical efficiency it should be possible to enhance the efficiency of solar cells significantly. However, the actual quantum efficiency of this system is rarely reported. Most likely this is due to the difficulty of quantifying the UV excitation as well as the visible and NIR emission in such a large range, in addition to the challenges associated with synthesizing high quality materials. The only report to the author's knowledge is from Xu *et al.* who determined the quantum efficiency of Bi and Yb doped YVO_4 , obtaining a quantum efficiency of 12.3% for $\text{YVO}_4:\text{Bi}_{0.05}\text{Yb}_{0.10}$.²² As optimizing quantum efficiencies is extremely demanding, this value should be considered to be reasonable at this stage, and further optimization could yield efficiencies far beyond this.

In this study we investigate optical and structural properties of $\text{YVO}_4:\text{Yb}^{3+}$ thin films deposited by atomic layer deposition (ALD) and attempt to measure the quantum efficiency of the produced films. ALD is a unique gas-phase deposition technique and is considered a powerful method for depositing thin and conformal films, with fine control of the atomic distribution.²³ In our previous study on luminescent YbVO_4 by ALD,²⁴ we showed that, while the as-deposited films are amorphous, it is possible to achieve high quality crystals by post deposition annealing, and thus expect the same to hold true for the $\text{YVO}_4:\text{Yb}^{3+}$ system. As

ALD has already been adopted by the solar cell industry for surface passivation, the addition of a conversion layer made by the same technique should be easily incorporated in the production process if it can be used to improve solar cell efficiencies.

Experimental

The Y-Yb-V-O films were deposited with an F-120 research-type ALD-reactor (ASM Microchemistry Ltd) at a reactor pressure of ~2.8 mbar and at a deposition temperature of 260, 290 and 300 °C for three different sets of samples that will be described later. Samples deposited at 310 °C did not exhibit self-limiting growth. The β -diketonate chelate Yb(thd)₃ (thd=2,2,6,6-tetramethyl-3,5-heptanedione) (Strem Chemicals, >99.9%), was used as the ytterbium precursor, while VO(thd)₂ and Y(thd)₃ were used as the vanadium and yttrium precursor and were synthesized in-house as described in Refs ^{25,26}, respectively. YCl₃·6H₂O (Sigma-Aldrich, >99.99%) was used as the yttrium source material for the Y(thd)₃ precursor. Ozone was used as the oxygen source and was produced from >99.9% O₂ in an In USA ozone generator (AC-2025). Nitrogen was used as both carrier and purge gas and was separated from air in a nitrogen generator (Schmidlin UHPN3001 N₂ purifier, >99.999% N₂ + Ar purity). All depositions were preceded by an *in situ* 10 minute ozone cleaning consisting of 100 cycles of 1.5 seconds O₃ pulse and 4.5 seconds N₂ purge at the deposition temperature in order to remove any organic remains while letting the reactor temperature stabilize.

Yb(thd)₃, Y(thd)₃ and VO(thd)₂ were all sublimated at 128 °C. Pulse durations were 3/3/3 seconds for (Yb(thd)₃, Y(thd)₃, VO(thd)₂)/purge/O₃/purge, for the deposition of Yb₂O₃, Y₂O₃ and V₂O₅ layers, and all parameters were determined to be well within saturating conditions.

All the Si (100) and SiO₂ substrates used for the depositions were laser cut. The thickness of the native oxide layer on the silicon substrates ranged from 2-4 nm and was measured by spectroscopic ellipsometry before each deposition.

For depositions at 260 and 290 °C, the following substrates were used: one 3×3 cm² Si substrate for X-ray fluorescence purpose, ten 0.5×0.5 cm² Si substrates for annealing purposes and photoluminescence/excitation measurements, and two 4×0.5 cm² Si substrates placed at the back and front of the reaction chamber to monitor the conformality of the films across the whole chamber. For most of the depositions a ~2×2 cm² silica substrate was placed vertically, parallel to the flow direction, to be used in absorption and quantum efficiency measurements.

The samples were annealed post deposition in air at 400-1000 °C in intervals of 100 °C in a tube furnace. The samples were placed inside a quartz ampoule that was open in the cold end of the furnace. They were placed in the furnace at ambient temperatures and heated to the desired temperature at a rate of ca. 240 °C/h and extracted from the hot furnace after 1 hour. The silica substrates were annealed at 1000 °C for 1 hour. All figures in the first section of this study refer to samples deposited at 260 °C, using 56 pulse% VO(thd)₂ and varying the Y(thd)₃/Yb(thd)₃ pulse ratio, and annealed at 1000 °C for 1 hour, unless stated otherwise.

In order to investigate if it is possible to keep an as-deposited layered doping profile (Y³⁺/Yb³⁺) into the crystalline phase, two

samples were deposited where the pulsed stoichiometry between VO(thd)₂ and Ln(thd)₃ was 1:1, but instead of alternating between Y(thd)₃ and Yb(thd)₃, several consecutive pulses of each were deposited in order to create layered materials. The samples were deposited at 300 °C. One of the multi-layered samples was deposited using a superstructure of 25 consecutive pulses of Y(thd)₃/O₃/VO(thd)₂/O₃ followed by 25 consecutive pulses of Yb(thd)₃/O₃/VO(thd)₂/O₃ (termed 25:25), and another was deposited using a 100:100 pulse ratio between Y(thd)₃ and Yb(thd)₃. The layer thicknesses were selected so that it was possible to detect them with XRR. The samples were deposited at 300 °C. The resulting films had total thicknesses of 115 nm and 110 nm for 25:25 and 100:100, respectively.

The crystallinity of all the samples was determined by X-ray diffraction (XRD), using a Bruker D8 Discovery X-ray diffractometer with CuK_{α1} radiation and a Ge(111) monochromator. The chemical composition was determined by X-ray fluorescence (XRF) on a PANalytical Axios minerals max spectrometer and interpreted with the Omnian and Stratos analysis software. Note that this technique determines the ratio between the various cations in the sample and the data is plotted as cat%. For the crystalline samples it is more common to use mol% Yb in the samples, which will generally be double the amount of cat% determined from the XRF data when the stoichiometry of Yb₂O₃ is taken as basis. In order to avoid confusion and to use the most precise value, pulse% Yb(thd)₃ will be used to describe the samples. 1 pulse% Yb(thd)₃ corresponds to 1 Yb(thd)₃/O₃ cycle per 100 total cycles of Y(thd)₃/O₃, Yb(thd)₃/O₃ and VO(thd)₂/O₃. Pulse% Y(thd)₃/Yb(thd)₃/VO(thd)₂ will from here on be abbreviated p% Y/Yb/VO in the text.

The film thickness was determined with a J. A. Woollam alpha-SE ellipsometer in the 380-890 nm range. The Cauchy-model was used to parameterize the ellipsometry experimental data. Photoluminescence (PL) measurements in the visible range were performed with a 325 nm, CdHe laser and an OceanOptics USB4000 photospectrometer, while an Edinburgh Instruments FLS920 fluorescence spectrometer was used for recording excitation spectra and emission spectra in the NIR, using a 450 W Xe lamp as excitation source and a liquid-nitrogen cooled Hamamatsu R5509-42 PMT. The detectors were not calibrated. PL decay measurements were recorded with the same spectrometer as the excitation measurement and excited using a 270 nm diode. The visible emission was detected using a Hamamatsu R928 PMT. An optical parametric oscillator (OPO) system (Opotek HE 355 II) pumped by the third harmonic of a Nd:YAG laser was used as excitation source for the NIR emission. The OPO system was set at $\lambda_{\text{exc}} = 355$ nm, with a repetition rate of 20 Hz. The PL decay was recorded with the same equipment used for the excitation measurement.

The quantum efficiency measurements were performed on samples deposited on fused silica substrates, using an integrating sphere, while using the same equipment as for the excitation measurements. All measurements were carried out at room temperature.

A Hitachi SU8230 field emission scanning electron microscope (FE-SEM) was used to study the surface morphology of a selection of the samples. The X-ray reflectivity (XRR) measurements were performed with a PanAlytical Empyrean

diffractometer with a parallel beam mirror as primary optics, a 0.27° parallel collimator with 0.04 rad soller slits as secondary optics and a proportional Xe-detector. The samples were annealed *in-situ* with an Anton Paar DHS 1100 domed hot stage for 10 minutes in intervals of 50°C from 300 – 800°C , and were cooled down to 25°C during the measurements before being annealed at the next temperature.

Results and Discussion

The deposition rate of Yb_2O_3 and V_2O_5 was previously discussed in our study on YbVO_4 .²⁴ The deposition rate of Y_2O_3 and YVO_4 at 260°C was determined to be ~ 13 pm/c and ~ 17 pm/c, respectively. An overview of the thickness (from ellipsometry) and growth rate of the various samples in this study is provided in Table S1.

In our previous study we determined that crystallization of YbVO_4 could be accelerated in a flux of excess V_2O_5 due its low melting point (690°C), and that the emission intensity was strongly correlated with crystallinity. In order to determine the optimal pulse composition with respect to emission intensity for the $\text{YVO}_4\text{:Yb}^{3+}$ system, samples with 4 p% Yb and varying $\text{Y}(\text{thd})_3/\text{VO}(\text{thd})_2$ pulse ratios were deposited and annealed at 1000°C . The XRF results for these samples are given in Figure S1, while the total NIR-emission intensity of each sample is shown in Figure S2.

The results once again indicate that an excess of V_2O_5 aids in the crystallization process, resulting in higher PL intensities, with the 56 p% $\text{VO}(\text{thd})_2$ sample displaying the highest emission intensity. This was consequently used for the deposition of $\text{YVO}_4\text{:Yb}^{3+}$ at 260°C , while the $\text{Y}(\text{thd})_3$ and $\text{Yb}(\text{thd})_3$ pulse ratios were varied. Note that differences in absorption have not been taken into account and samples with higher pulse% $\text{VO}(\text{thd})_2$ are expected to be more transparent after annealing due to crystallization resulting in reduced surface coverage. The quantum efficiency of the samples with more than 56 p% $\text{VO}(\text{thd})_2$ could thus be similar or higher than the ones with 56 p%.

A set of samples were deposited at 290°C in order to determine whether the deposition temperature could influence the optical properties after annealing. As the deposition rate of V_2O_5 is sensitive to the deposition temperature²⁷ compared to Yb_2O_3 and Y_2O_3 , the pulse rate was adjusted in order to obtain similar samples. A 1:1 pulse rate between $\text{VO}(\text{thd})_2$ and $\text{Yb}/\text{Y}(\text{thd})_3$ yielded the same $\text{Ln}_2\text{O}_3\text{:V}_2\text{O}_5$ ratio as samples deposited at 260°C , as shown in Figure 1. Figure S3 shows that the PL intensity was more or less unaffected by the change in deposition temperature when the pulse rate was varied to compensate for the increased deposition rate of V_2O_5 at 290°C . Thus in the following discussion only samples deposited at 260°C will be considered, but apart from some slight variations the results are also valid for samples deposited at 290°C .

The normalized excitation spectrum monitoring the 983 nm emission of Yb^{3+} and the normalized visible and NIR emission spectra of a sample with 1 p% Yb are presented in Figure 2. The spectra resemble that of YbVO_4 from our previous study,²⁴ and the energy transfer processes are expected to be the same as described there. Of note is that the NIR emission (900–1100 nm) can only be explained by a CET process, which would imply that

Figure 1: Cat% vs. p% Yb as determined by XRF for samples deposited at 260 and 290°C . The samples deposited at 260°C were deposited using 56 p% $\text{VO}(\text{thd})_2$ while varying the $\text{Y}(\text{thd})_3/\text{Yb}(\text{thd})_3$ pulse rate, while for the samples deposited at 290°C , 50 p% $\text{VO}(\text{thd})_2$ was used to compensate for the increased growth rate of V_2O_5 relative to Y_2O_3 and Yb_2O_3 at this temperature.

Figure 2: Normalized PLE spectrum (blue) monitoring the 983 nm emission of Yb^{3+} and normalized PL spectra (green/red) of an $\text{YVO}_4\text{:1 p% Yb}$.

down conversion takes place. The additional peaks are due to Dy^{3+} (483 and 573 nm) and Eu^{3+} (617 and 700 nm) impurities in the $\text{Y}(\text{thd})_3$ precursor. Thin films synthesized by using the 98+% $\text{Y}(\text{thd})_3$ (3N Y) precursor from Strem produced significantly stronger signal from various lanthanide impurities (Figure S4), though notably the Yb^{3+} emission was also enhanced in these samples. This is possibly due to the $\text{Y}(\text{thd})_3$ from Strem having a higher chemical purity towards lighter elements, resulting in less carbon impurities in the films, but appears to contain more impurities from other lanthanides than the 4N source material used to synthesize the in house-made $\text{Y}(\text{thd})_3$. Samples made with $\text{Y}(\text{thd})_3$ from Strem did not exhibit a reproducible emission spectrum across the whole film after annealing and not between two identical depositions, due to significant variation in the

amounts of impurities. For this reason home-made $\text{Y}(\text{thd})_3$ was used for the samples where structural and optical properties were compared.

Figure 3 shows that all the samples crystallize into the YVO_4 crystal structure after annealing at 1000 °C (Crystallographic open database No. 9011137²⁸). The intensity of the (200) and (400) reflections increase with increased Yb-concentration, indicating that these orientations become more preferred at higher doping levels.

The total visible and NIR emission from the annealed samples are presented in **Figure 4**. The visible emission decreases with increased $\text{Yb}(\text{thd})_3$ pulsing due to more energy being transferred from $(\text{VO}_4)^{3-}$ to Yb^{3+} . The NIR-emission increases up to 4 p% Yb, which according the elemental analysis from XRF corresponds to ~8 mol% Yb^{3+} , which is in perfect agreement with calculations performed by Wei *et al.*¹¹ However, this concentration is twice as high as what has previously been observed experimentally for powders¹¹ or pulsed laser deposited films¹² of the same material. The reduction in NIR-emission is attributed to concentration quenching¹¹. The absorption spectra in

Figure 3: XRD of samples with 0-8 p% Yb.

Figure 4: Total PL counts in NIR and VIS region for samples deposited at 260 °C and annealed at 1000 °C.

Figure S5 show only slight differences in absorption and this is consequently not expected to significantly impact the detected emission in these samples. The deposition temperature did not notably affect the emission intensities, as shown in **Figure S3**.

Figure 5 shows PL decay measurements monitoring the NIR emission of samples with 2-8 p% Yb, fitted to a single exponential function. The obtained values for the lifetime are in near perfect agreement with similar measurements for $\text{YVO}_4:\text{Yb}^{3+}$ powders.¹¹ The lifetime decreases with increased p% Yb, which is attributed to concentration quenching. The lifetime of samples with the same p% Yb, but varying p% V and Y, is provided in **Figure S6**, and appears to be more or less constant for different V/Y ratios. It is thus evident that only the Yb-concentration has a significant effect on the observed lifetime.

The lifetime of the visible emission of samples with 0-4 p% Yb is shown in **Figure 6**. The instability of the diode used in the measurement caused a smearing of the data, though the relative detected emission between the samples should still provide quantitative data. It is evident that increasing the Yb^{3+}

Figure 5: PL decay measurements of the Yb^{3+} emission at 983 nm for samples with 2-8 p% Yb, deposited at 260 °C and annealed at 1000 °C.

Figure 6: PL decay measurements of the $(\text{VO}_4)^{3-}$ emission at 430 nm for samples with 2-8 p% Yb, deposited at 260 °C and annealed at 1000 °C.

concentration reduces the $(\text{VO}_4)^{3-}$ lifetime, in agreement with previous studies,^{11,12} which can be explained by introduction of the extra decay pathway via Yb^{3+} , which is strong evidence for CET taking place.

In order to get a rough estimate on the maximum theoretical quantum efficiency of a phosphor, it is common to compare the integrated intensity of lifetime measurements of samples with and without a luminescent dopant. The CET efficiency, η_{CET} , and the theoretical quantum efficiency, η_{QE} , can be determined from the following equations:²⁹

$$\eta_{\text{CET}, x \text{ p\% Yb}} = 1 - \frac{\int I_{x \text{ p\% Yb}} dt}{\int I_{0 \text{ p\% Yb}} dt},$$

$$\eta_{\text{QE}} = \eta_{\text{VO}_4} (1 - \eta_{\text{CET}}) + 2\eta_{\text{Yb}} \eta_{\text{CET}},$$

where I is the decay intensity, $x \text{ p\% Yb}$ indicates the Yb content in the sample, and η_{VO_4} and η_{Yb} correspond to the luminescence quantum efficiency of $(\text{VO}_4)^{3-}$ and Yb^{3+} , respectively. For the samples with 2, 4 and 8 p% Yb the η_{CET} was determined to be 34%, 44% and 50%, respectively. These values are significantly lower than what has been found for $\text{YVO}_4:\text{Yb}^{3+}$ powders,¹¹ but slightly higher than what has been reported for thin films made by pulsed laser deposition.¹² By ignoring all quenching processes and setting the luminescence quantum efficiencies of $(\text{VO}_4)^{3-}$ and Yb^{3+} to 1, an upper-limit of the value on the theoretical quantum efficiency for the samples with 2, 4 and 8 p% Yb is 134%, 144% and 150%.

The actual quantum efficiency of a sample with 1 p% Yb was found to be only ~15%. Due to the samples emitting in the NIR, while excitation takes place in the UV, two different detectors had to be employed and the results had to be correlated by using an overlapping region where both detectors had a reasonable response. A more detailed description of the measurement is provided in the supplementary data file S9. The sample with 4 p% Yb was unfortunately not measured, but comparison of the PL intensities suggests that it could have a quantum efficiency above 15%. The measured quantum efficiency can only be considered a rough estimate, though it is clear that the efficiency is far from the >100% required to significantly enhance the efficiency of solar cells. In a sample with only 1 p% Yb, the concentration quenching is not expected to be substantial, so the large discrepancy between the theoretical and observed quantum efficiency is most likely due to the poor quantum efficiency of $(\text{VO}_4)^{3-}$ in these samples. In the theoretical upper-limit approximation, the efficiency of $(\text{VO}_4)^{3-}$ is set to 100%, but according to the QE measurement it is only around 5% due to the $^3\text{T}_{1,2} \rightarrow ^1\text{A}_1$ transitions being spin-forbidden and thus easily quenched. Optimizing quantum efficiencies for this system is extremely challenging, e.g. $\text{YVO}_4: 5 \text{ mol\% Eu}^{3+}$ can have quantum efficiencies up towards 70%,³⁰ yet most reports in the literature are far below this, e.g. Singh *et al.* measured only 9% for the same Eu^{3+} concentration.³¹ Avoiding the quenching of $(\text{VO}_4)^{3-}$ is the key to realizing high quantum efficiencies, and using source materials and synthesis methods that produce the highest quality crystals should thus be prioritized when aiming for this.

A FE-SEM image revealing crystals with distinct facets and

high crystal quality, made with the $\text{Y}(\text{thd})_3$ precursor from Strem Chemicals can be found in Figure S7. Figure S4 shows that the NIR emission of this sample is significantly higher than that of the most emissive sample made with in-house produced $\text{Y}(\text{thd})_3$ at this excitation wavelength, despite being highly transparent due to only around 25% of the sample being covered by $\text{YVO}_4:\text{Yb}^{3+}$. The strong impurity signal from various lanthanides in this sample is also an indication that the energy transfer from $(\text{VO}_4)^{3-}$ is highly efficient. While we have yet to reproduce a sample with similar emission intensities on fused silica, it is our interpretation that the quantum efficiency of this sample is much higher than 15%, though due to being highly transparent it would not be useful as a conversion material in its current state. However, the results indicate that there are reasons to be optimistic with respect to eventually use $\text{YVO}_4:\text{Yb}^{3+}$ to increase the efficiency of solar cells.

Layered $\text{YVO}_4:\text{YbVO}_4$

One of the advantages of ALD is the possibility of making layered materials, which could for instance be functionally similar to core-shell structures of nanoparticles.³²⁻³⁵ These are interesting due to their tuneable properties and can be used to facilitate energy transfer between materials exhibiting undesirable charge-transfer states when in direct proximity to each other by using an intermediate shell to separate them. In order to create a functionally similar kind of material by ALD it would require a sub-nanometre doping profile of crystalline material. However, crystallizing the samples deposited at 260-290 °C causes the film-structure to collapse and the as-deposited doping profile is lost, as shown in Figure 7 for a sample with 1 p% Yb annealed at 1000 °C. In order to make a crystalline layered material, we wanted to determine the temperature at which the individual layers merge, and whether there is a temperature at which it is possible to crystallize the material while maintaining the thin film structure and the as-deposited doping profile.

Two samples were deposited at 300 °C, which was previously determined to be the highest deposition temperature at which self-limiting growth takes place for this system. One sample was deposited with 0.9-1 nm thick YVO_4 and YbVO_4 layers, and

Figure 7: FE-SEM image of a sample with 1 p% Yb annealed at 1000 °C.

another was deposited with 3.6-3.8 nm thick layers, according to XRR data presented in **Figure 8**. XRD revealed that the samples were crystalline already as deposited, as shown in **Figure 9**, proving that it is indeed possible to deposit crystalline layers of YVO_4 and YbVO_4 in a very narrow temperature range around

Figure 8: XRR measurements of samples with 25:25 (top) and 100:100 (bottom) cycle sequence of $\text{Y}(\text{thd})_3/\text{O}_3/\text{VO}(\text{thd})_2/\text{O}_3$ and $\text{Yb}(\text{thd})_3/\text{O}_3/\text{VO}(\text{thd})_2/\text{O}_3$. Top sample has layer thicknesses of 0.9-1.0 nm, while the bottom sample has layer thicknesses of 3.6-3.8 nm.

Figure 9: XRD of a samples with 25:25 and 100:100 pulse ratio of $\text{Y}(\text{thd})_3/\text{O}_3/\text{VO}(\text{thd})_2/\text{O}_3$ and $\text{Yb}(\text{thd})_3/\text{O}_3/\text{VO}(\text{thd})_2/\text{O}_3$, as-deposited and after annealing for 1 hour at 1000 °C.

300 °C. The increased XRD intensity indicates that the crystallinity, and hence the luminescence efficiency, can still be increased by post-deposition annealing. The sample with ~1 nm thick layers could be heated up to 750 °C before the XRR multilayer feature was completely dominated by noise and no clear peak could be observed. The sample with slightly less than 4 nm thick layers, on the other hand, still showed detectable layers at 800 °C, which FE-SEM also confirmed to still be a cohesive film at this point (**Figure S8**). It thus appears to be possible to preserve the as-deposited doping profile at slightly higher temperatures by increasing the layer thickness.

As Yb^{3+} is chemically similar to most of the other rare earth elements, the results indicate that it should be possible to deposit a layered $\text{LnVO}_4:\text{YVO}_4$ material with sub-nanometre layer thicknesses in order to create complex structures with highly tuneable optical properties by using the ALD technique.

Conclusion

It has been shown that controlled deposition of $\text{YVO}_4:\text{Yb}^{3+}$ is possible with ALD at deposition temperatures between 260-300 °C, and that the films can act as UV to visible and NIR converters after annealing. The energy transfer from $(\text{VO}_4)^{3-}$ to Yb^{3+} in the annealed samples is lower than what has been reported for powders, but slightly higher than what has been reported for thin films of the material made by other deposition techniques. The strongest NIR emission at an excitation wavelength of 325 nm was detected in a sample with 4 p% Yb, corresponding to ~ 8 mol% Yb^{3+} and the upper-limit theoretical efficiency of the sample was determined to be 144%. The actual quantum efficiency of a sample with 1 p% Yb was determined to be approximately 15%. By using different or higher grade precursors and optimizing the deposition and annealing conditions, it is our interpretation that substantially higher quantum efficiencies can be realized, and that it eventually can be useful as a conversion layer for enhancing the efficiency of solar cells, or for other applications where efficient UV-NIR conversion is desired.

It has been determined that depositing $\text{YVO}_4:\text{Yb}^{3+}$ at 260-290 °C by ALD results in amorphous films that can be crystallized by post-deposition annealing. A surplus of V_2O_5 above the melting point of V_2O_5 accelerates the crystallization process, but also causes the films to collapse and crystallize into micron-sized grains. Deposition of $\text{YVO}_4:\text{Yb}^{3+}$ at 300 °C results in crystalline films and the crystallinity can be further increased by post-deposition annealing. The temperature at which the as-deposited doping profile of layered $\text{YbVO}_4:\text{YVO}_4$ can be maintained depends on the layer thickness. For samples with ~1 nm layer thickness the as-deposited doping profile can be maintained up to 750 °C. As Yb^{3+} can be replaced by most of the trivalent lanthanides, the results indicate that it should be possible to deposit a crystalline $\text{LnVO}_4:\text{YVO}_4$ layered material by ALD, using several different lanthanides. This is promising with respect to design of advanced layered optical structures with tuneable properties by ALD in the future.

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Notes and references

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Supplementary

Table S1a: Number of cation cycles, thickness and growth rate for films deposited at 260 °C, with 4 p% Yb(thd)₃ and varying p% VO(thd)₂ and Y(thd)₃.

Pulse% VO(thd) ₂	# Cycles	Thickness (nm)	Growth rate (pm/c)
44	5250	86	16.4 pm/c
48	5100	83	16.3 pm/c
52	5100	77	15.1 pm/c
56	5000	80	16.0 pm/c
60	5200	77	14.8 pm/c

Table S1b: Number of cation cycles, thickness and growth rate for films deposited at 260 °C, with 56 p% VO(thd)₂ and varying p% of Y(thd)₃ and Yb(thd)₃

Pulse% Yb(thd) ₃	# Cycles	Thickness (nm)	Growth rate (pm/c)
0	5200	87	16.7 pm/c
1	5200	81	15.6 pm/c
2	5000	78	15.6 pm/c
4	5200	80	15.4 pm/c
6	5000	75	15.0 pm/c
8	5000	80	16.0 pm/c

Table S1c: Overview of number of cation cycles, thickness and growth rate for films deposited at 290 °C, with 50 p% VO(thd)₂ and varying p% of Y(thd)₃ and Yb(thd)₃

Pulse% Yb(thd) ₃	# Cycles	Thickness (nm)	Growth rate (pm/c)
0	5200	112	21.5 pm/c
1	5200	108	20.8 pm/c
2	5200	107.5	20.6 pm/c
4	5200	105.5	20.3 pm/c
6	5200	104	20.0 pm/c

Figure S1: Cat% vs. p% VO(thd)₂ as determined by XRF for samples deposited at 260 °C and a fixed 4 p% Yb(thd)₃.

Figure S2: Total PL intensity detected in the NIR region vs. p% VO(thd)₂ for samples deposited at 260 °C, with a fixed 4 p% Yb and annealed at 1000 °C for 1 hour.

Figure S3: Total PL intensity detected in the NIR region vs. annealing temperature for samples with 1 p% Yb, deposited at 260 °C and 290 °C.

Figure S4: Comparison between samples with Y(thd)₃ precursor from Strem Chemicals (green) and home-made (blue). The red spectrum shows that samples without any yttrium do not exhibit peaks from impurities.

Figure S5: UV-Vis measurements of samples with 1-8 p% Yb deposited on fused silica at 260 °C and annealed at 1000 °C.

Figure S6: PL decay measurement of samples with 4 p% Yb and varying pulse% VO(thd)₂ and Y(thd)₃.

Figure S7: FE-SEM images of samples with 75 p% VO(thd)₂, 21 p% Y(thd)₃ and 4 p% Yb(thd)₃, deposited with Y(thd)₃ precursor from Strem Chemicals and responsible for the PL emission (green) in Figure S2.

Figure S8: A sample with slightly less than 4 nm layers of YVO₄:YbVO₄ annealed at 800 °C for 10 min.

S9: Quantum Efficiency Measurement

The quantum efficiency of the YVO_4 : 1 p% Yb phosphor was determined by using the overlapping spectral region of 795-825 nm of the two PMTs used to detect the visible and NIR emission. The emission of the Xe lamp was recorded with each detector at three different wavelengths using the same slits within this region and corrected using the correction file for the integrating sphere and the two detectors. Comparing the total recorded emission revealed a strong correlation between the two measurements, i.e. the PMT used to record visible emission is ~4.6 times more sensitive after taking the correction files into account. In order to compare the emission recorded by the two detectors, the emission detected by the NIR detector was multiplied by 4.6. The quantum efficiency measurement could then be conducted normally by measuring the UV emission escaping the sphere with and without the sample, followed by measuring the escaped visible and NIR emission and calculating the fraction of the absorbed UV light that produces emission.