Giedraityte, Z.; Sundberg, Pia; Karppinen, Maarit

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1. Introduction

Motivation for the synthesis of various Eu-based inorganic-organic complexes stems from their good photoluminescence properties in the visible range relevant to various optical applications. Luminescent europium complexes act as light conversion molecular devices, and offer an attractive substitute for the commonly used organic fluorophores due to their photochemical stability, long luminescence lifetimes and sharp emission peaks. The Laporte-forbidden transitions of europium causing weak excitation of electrons are overcome by using a sensitizing chromophore or antenna as a ligand in the europium complexes. Various N-heterocyclic ligands including pyridine, phenanthroline, benzimidazole, pyrazole, oxazoline, hydroxylquinoline, azaxanthone, etc., have been employed as efficient sensitizing chromophores for the photoluminescence of europium; in particular, aromatic pyridine ligands are good candidates for enhancing the luminescence properties of Eu and other lanthanides due to their strong binding abilities to the metal constituent. Inorganic-organic hybrid materials have good luminescent properties and play a key role in many important optical applications, such as nanosized phosphorescent and optoelectronic devices. Here we demonstrate the feasibility and potential benefits of synthesizing such materials with a direct deposition method with atomic/molecular layer precision using the emerging atomic layer deposition/molecular layer deposition (ALD/MLD) technique. Such a process allows for fundamental new types of highly uniform and conformal hybrid inorganic-organic thin films by alternating exposures of inorganic and organic reactants on flexible/sensitive/nanstructured surfaces. We employ Eu(thd)$_2$ and 3,5-pyridinedicarboxylic acid as precursors and deposit the films on a variety of substrate materials in the temperature range from 240 to 400 °C. The appreciably fast self-limiting surface reactions yield thin films with high luminescence intensities.

We foresee that our Eu-hybrid thin-film phosphors grown by ALD/MLD could be exciting new phosphor materials in applications where ultrathin luminescent coatings on flexible and/or nanostructured surfaces are needed.

Flexible inorganic-organic thin film phosphors by ALD/MLD

Z. Giedraityte, P. Sundberg and M. Karppinen

Inorganic-organic europium-based hybrid materials have good luminescent properties and play a key role in many important optical applications, such as nanosized phosphorescent and optoelectronic devices. Here we demonstrate the feasibility and potential benefits of synthesizing such materials with a direct deposition method with atomic/molecular layer precision using the emerging atomic layer deposition/molecular layer deposition (ALD/MLD) technique. Such a process allows for fundamentally new types of highly uniform and conformal hybrid inorganic-organic thin films by alternating exposures of inorganic and organic reactants on flexible/sensitive/nanstructured surfaces. We employ Eu(thd)$_2$ and 3,5-pyridinedicarboxylic acid as precursors and deposit the films on a variety of substrate materials in the temperature range from 240 to 400 °C. The appreciably fast self-limiting surface reactions yield thin films with high luminescence intensities.

We foresee that our Eu-hybrid thin-film phosphors grown by ALD/MLD could be exciting new phosphor materials in applications where ultrathin luminescent coatings on flexible and/or nanostructured surfaces are needed.
excellent luminescence properties fabricated from Eu(thd)$_3$ (thd: 2,2,6,6-tetramethyl-3,5-heptanediene) and 3,5-pyridinedicarboxylic acid precursors. The underlining surface reactions are shown to be self-limiting, thus providing a means to deposit highly uniform and conformal coatings with precise control over thickness on various substrates. A schematic illustration of the ideal bonding structure of these films is given in Fig. 1.

Fig. 1. Illustration of a possible structure of our ALD/MLD-grown Eu-hybrid thin films.

2. Experimental section

The ALD/MLD thin-film depositions were performed in a commercial ALD reactor (F-120 by ASM Microchemistry Ltd.). The inorganic precursor Eu(thd)$_3$ was prepared in-house, while the organic precursor, 3,5-pyridinedicarboxylic acid, was a commercial product (TCI Europe N.V.). During the depositions, both the Eu(thd)$_3$ and the pyridinedicarboxylic acid precursors were kept in glass crucibles inside the reactor, at 140 and 200-235 °C, respectively. Due to the high volatility of the organic precursor, the latter crucible was covered with quartz glass wool (Nabertherm). Nitrogen (>99.999%; Schmidlin UHPN 3000 N$_2$ generator) was used as a carrier and purging gas, and a pressure of 2 to 4 mbar was maintained in the reactor during the film deposition.

The film thickness values were determined by X-ray reflectivity measurements (XRR; PANalytical X’Pert MPD Pro Alfa 1). Grazing incident X-ray diffraction measurements with the same instrument were carried out to investigate the crystallinity of the samples. Fourier transform infrared spectroscopy (FTIR; Nicolet Magna 750) was used to identify the organic components in the samples. The measurement chamber was purged with dry air, and the spectrum measured for the substrate was subtracted from those for the thin-film samples. The surface chemistry of the films was investigated by using X-ray photoelectron spectroscopy (XPS; AXIS Ultra by Kratos Analytical) with monochromated Al-Kα irradiation at 100 W and the charge neutralizer on. Finally the films were characterized with monochromated Al-Kα photoelectron spectroscopy (XPS; AXIS Ultra by Kratos) and Fourier transform infrared spectroscopy (FTIR; Shimadzu IR Prestige-21).

3. Results and discussion

In our preliminary deposition experiments we first searched for the optimal precursor/purge pulse lengths; the surface reactions were found to be appreciably fast, resulting in the same growth-per-cycle (GPC) value (within experimental error limits) at a given deposition temperature independent of the pulse lengths of the precursors – a fact that is generally taken as a proof of the saturated self-limiting nature of the reactions; we showed this at the deposition temperature of 290 °C for the pulse length ranges of 1 – 5 s for Eu(thd)$_3$ and 1 – 10 s for pyridinedicarboxylic acid. For the further experiments we then fixed precursor/purge pulse lengths as follows: 1-s Eu(thd)$_3$/2-s N$_2$/2-s pyridinedicarboxylic acid/4-s N$_2$. It was also confirmed that the films nucleated and grew in a similar manner on various substrate materials such as silicon, quartz, borosilicate glass, PET-ITO, polyamides and others; note that e.g. PET-ITO was
selected because it is a commonly used flexible substrate in many applications and also readily commercially available. In Fig. 2 we plot the growth-per-cycle (GPC) values at different deposition temperatures calculated from the resultant film thickness values determined by XRR measurements. It is seen that as is typical for the inorganic-organic hybrid materials grown by ALD/MLD the thickness decreases with increasing deposition temperature.\textsuperscript{22} For the film quality an optimum deposition temperature range was estimated to be between 260 and 340 °C, but homogeneous films were found to be formed even at temperatures down to 240 °C or up to 400 °C. In the inset of Fig. 2 we demonstrate the essentially ideal ALD/MLD behaviour, i.e. linear dependency of the film thickness on the number of ALD/MLD cycles, for films deposited at 300 °C.

![Fig. 2. Growth per cycle (GPC) at different deposition temperatures for the present Eu-hybrid thin films; the inset shows the total film thickness as a function of number of deposition cycles for films deposited at 300 °C. Experimental error bars are estimated to be within the datum point square marks.](image)

Our Eu-hybrid films were amorphous from XRD measurement (not shown here). They were confirmed to be essentially pure from XPS data, with the following approximate elemental compositions: 62 % C, 25 % O, 6 % N, 7 % Eu, which are in reasonable agreement with the suggested film structure (Fig. 1). The films were shiny in appearance, and could be handled and stored in ambient air for a year without side reactions. From heat-treatment experiments carried out in an N\textsubscript{2} gas flow it was confirmed that the films remained stable at temperatures at least up to 500 °C.

In Fig. 3(a) we display FTIR spectra for a representative Eu-hybrid thin-film sample and for a free 3,5-pyridinedicarboxylate ligand for comparison; the spectrum for the Eu-hybrid film is perfectly consistent with the schematic structure (Fig. 1). The v(C=O) (-COOH) stretching frequency of the free 3,5-pyridinedicarboxylate ligand at 1700 cm\textsuperscript{-1} is absent in the spectrum of the Eu-hybrid film. The characteristic peak for v(C=O) is observed at 1396 cm\textsuperscript{-1}. This frequency implies that the oxygen atoms of the carboxylate groups are coordinated to the Eu\textsuperscript{3+} ion. The stretching vibrations of the C=N bond in the pyridine ring are shifted to 1602 cm\textsuperscript{-1} and 1551 cm\textsuperscript{-1} for the Eu-hybrid film indicating that pyridine participates in the coordination to europium.\textsuperscript{24–28} The absence of the broad absorption band at 3200-3500 cm\textsuperscript{-1} confirms that the Eu-hybrid film is devoid of OH and NH bonds, as expected. The XPS high-resolution regional spectrum of N 1s signal (Fig. 3(b)) for the same Eu-hybrid film sample is in line with our conclusions based on the FTIR data, that is, the spectrum shows a small but clear extra component (marked by asterisk in Fig. 3(b)) of a distinct chemical state for the Eu-hybrid in comparison to the spectrum for the free 3,5-pyridinedicarboxylate ligand, which could be attributed to the suggested N-Eu=O bond, although this is only one possible interpretation.

![Fig. 3. (a) FTIR spectra, and (b) N-XPS spectra for 3,5-pyridinedicarboxylic acid (top) and a 100-nm thick Eu-hybrid thin film deposited at 290 °C (bottom).](image)
some unique systems for which the triplet state lies below the emitting state.\textsuperscript{32}

![UV-vis spectrum](image)

Fig. 4. UV-vis spectrum for a 100-nm thick Eu-hybrid thin film deposited at 290 °C on a quartz substrate.

In Fig. 5 we display the photoluminescence excitation ($\lambda_{\text{em}} = 615$ nm) and emission ($\lambda_{\text{ex}} = 270$ nm) spectra for a 100-nm thick Eu-hybrid thin film deposited at 290 °C. The appearance of the intense excitation peak around 270 nm indicates the efficient repopulation of the excited states of the Eu$^{3+}$ ions by the electrons transferred from the pyridinedicarboxylic acid molecules. The photoluminescence emission spectrum exhibits the characteristic intense narrow bands from the $^5D_0 - ^7F_j$ transitions (where $J = 0-4$) of trivalent europium resulting in red light emission upon UV excitation. Most importantly, in the inset of Fig. 5 we show a photo taken under UV illumination from a Eu-hybrid film deposited on a flexible ITO-coated PET substrate; we can observe appreciably high europium emission intensity owing to the efficient energy transfer from the organic ligands. We also like to emphasize that measured the spectrum several times for the same sample after certain time periods to confirm that no visible differences occurred in the luminescence intensity with time.

![Photoluminescence spectrum](image)

Fig. 5. Photoluminescence excitation ($\lambda_{\text{em}} = 615$ nm) and emission ($\lambda_{\text{ex}} = 270$ nm) spectra for a 100-nm thick Eu-hybrid thin film deposited at 290 °C on a quartz glass substrate; the inset shows a photo taken under 270-nm UV illumination of a similarly deposited film on an ITO-coated PET substrate.

The PET-ITO substrate undergoes shrinkages at temperatures above 100 °C,\textsuperscript{33} and therefore the stress analysis was performed for thin-film coatings deposited on a new flexible polyimide DuPont Kapton that has tolerance for high temperatures as well as good light transmittance and flexibility;\textsuperscript{34} the coatings investigated were a 100-nm thick Eu-hybrid film and a purely inorganic ALD-grown 85-nm thick europium oxide film for reference. The depositions on polyimide substrates resulted in homogeneous films even at temperatures as high as 290 °C. No cracks were visible in our Eu-hybrid thin-film coating (Figs. 6a-6c) up to the maximum elongation point (44 %), neither there were observed any effects on its photoluminescence properties. In contrast to the case of the Eu-hybrid films, on the surface of the europium oxide reference film there was observed cracking propagation within increasing tensile elongation (Figs. 6d-6f).

No defects were observed for our Eu-hybrid thin films after they had been repeatedly stretched 30 times up to 3 % tensile elongation and bended 600 times according to the reference.\textsuperscript{35} Similarly, no differences in the red europium photoluminescence intensity were observed before and after stretching or bending (Fig. 7). Hence we could conclude that our luminescent Eu-hybrid films indeed are mechanically highly flexible, as expected.\textsuperscript{36,37}
Fig. 6. Optical microscope images for a 100-nm thick ALD/MLD Eu-hybrid thin-film coating deposited at 290 °C on a polyimide substrate after the following tensile elongations: (a) 2%; (b) 4%, and (c) 8%; and for a 85-nm thick ALD Eu₂O₃ coating after the following elongations: (d) 2%; (e) 4%, and (f) 8%.

Fig. 7. Photoluminescence emission (λₑₓ = 270 nm) spectra for a 100-nm thick Eu-hybrid thin film deposited at 290 °C on a polyimide substrate before and after stretching; the inset shows a photo taken of this Eu-hybrid coating on a transparent polyimide substrate under 270-nm UV illumination.

4. Conclusions

We have demonstrated that the currently emerging ALD/MLD gas-phase thin-film technique can be used for direct deposition of new type of europium-organic hybrid materials where the organic constituent efficiently sensitizes the luminescence of europium. Our proof-of-the-concept data are for a process where Eu(thd)₃ and 3,5-pyridinedicarboxylic acid are employed as precursors, but we expect that there will be a number of other organic molecules which could be combined with europium for further tailoring of the structural and luminescence properties.

Our Eu-hybrid thin films were revealed to be highly uniform and amazingly stable, and most importantly to show high luminescence intensities. Moreover, preliminary mechanical testings confirmed that they are also highly flexible. Since the ALD/MLD technique – owing to the self-limiting gas-surface reactions – inherently allows the deposition of conformal coatings on a variety of substrate surfaces, we foresee that our Eu-hybrid thin films could be beneficial for many cutting-edge applications that demand ultrathin but large-area luminescent coatings on flexible substrates.

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Notes and references

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