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Photochemically induced deposition of protective alumina coatings onto UV emitting phosphors for Xe excimer discharge lamps

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ABSTRACT

This work concerns the particle coating of the UV-C emitting phosphor YPO_4:Bi, targeting a stability enhancement of the phosphor material for Xe excimer lamp operation. To this end, the material is coated by the wide band gap material Al_2O_3. In order to obtain a thin and homogeneous coating layer, a novel process based on the photochemical cleavage of NaN_3 in water was developed. This results in a slow and continuous enhancement of the pH value due to ongoing NaOH formation, which results in the precipitation of $Al(OH)_3$ from an $Al_2(SO_4)_3 \times 18H_2O$ solution. It turned out that the obtained particle coatings are of much better quality, i.e. homogeneity, compared to coatings made from a wet-chemical homogeneous precipitation process. The morphology and electrochemical properties of Al_2O_3 coated YPO_4:Bi are discussed on the basis of optical spectroscopy, ESA measurements, and SEM/EDX investigations.

1. Introduction

Luminescent materials are widely applied in gas discharge lamps and displays, while most commonly Hg or Xe discharge is used as the source of UV radiation. Due to the harsh conditions in such an environment (ion or electron sputtering, VUV radiation, high electrical field strength etc.), many phosphors show a severe decline of their quantum efficiency during the rated lifetime of the respective device [1,2]. To enhance the lifetime and/or to decrease the efficiency loss, a commonly applied measure is a particle coating. Phosphors in plasma displays are e.g. coated either by α-Al_2O_3 or by MgO [3,4].

The problem of phosphor degradation is particularly severe in UV emitting discharge lamps, since the Stokes Shift between the excitation and emission band are small, which results in strong re-absorption due to tremendous spectral overlap. UV lamps for tanning purposes are therefore solely rated for 1000 h or less, since their UV-B/A ratio declines rather fast, which is caused by the phosphor degradation and enhanced re-absorption of emitted UV-B radiation [5]. Main cause for the enhanced re-absorption is the greyishing of the phosphors and thus the reduced reflectivity, in particular at the high energy edge. This finding led to the development of particle coatings on phosphors for UV emitting lamps, e.g. $BaSi_2O_5$:Pb or YPO_4:Ce. A major point is the band gap of the coating material, which must be large enough in order to avoid absorption of the incident UV radiation (Hg: 185.0 + 253.7 nm, Xe: 148 + 172 nm). An appropriate material is thus α-Al_2O_3, since its band gap is about 9.5 eV [6,7]. It exhibits a point of zero zeta charge (pzzc) at around pH 8.7, i.e. the material behaves alkaline in aqueous solution [8]. This is also advantageous for discharges, because a high pzzc means that the material supports the release of electrons subsequent to an electron impingement [9–11].

The main drawback of α-Al_2O_3 is the rather high temperature for phase formation and the need for the conversion of precipitated $Al(OH)_3$ into the oxide. A standard method is the pH enhancement of an Al^{3+} comprising solution, e.g. by means of cleavage of urea [12]. However, this technique was experienced to yield non-dense coatings, if not additional measures, e.g. the use of stabilizers, are taken.

Our approach in this work is to use an inorganic precursor for the pH enhancement, which can be cleaved by UV radiation and is thus able to yield a slow and continuous pH increase. This precursor is NaN_3 which is not stable upon radiation below 260 nm. By using NaN_3 in an aqueous acidic solution of Al^{3+}, the precipitation of $Al(OH)_3$ is induced by irradiating the solution with a Hg amalgam discharge lamp. The separated precipitate is converted into α-Al_2O_3 by a post-thermal treatment. This process was used in order to apply a particle coating onto YPO_4:Bi. The results are discussed with respect to the coating homogeneity and density as well as the effects on the phosphor particle pzzc which

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may lead to an improvement of the stability of such phosphor against the harsh conditions in Xe excimer discharge lamps.

2. Experimental

2.1. Chemicals

The UV-C emitting phosphor, Bismuth doped Yttrium Phosphate (YPO_4:Bi) was purchased from Tailorlux GmbH, Germany. Sodium Azide (NaN_3) was purchased from Aldrich in p.a. quality. The precursor for $Al(OH)_3$ deposition, Aluminiumsulfate Octadecyhydrate ($Al_2(SO_4)_3 \times 18H_20$) was drawn from VWR Chemicals. All coating reactions were carried out in deionised water. Acidification was provided using concentrated Sulfuric acid (95 wt%) purchased from VWR Chemicals.

2.2. Reactor setup

The particle coating procedures were carried out in a custom build reactor system. A picture is given in Fig. 1. The displayed system consists of a glass immersion-pipe UV reactor whose double wall quartz immersion pipe is equipped with a water cooled tubular 45 W Hg-NIQ discharge lamp. The reactor includes a magnetic stirring bar, propelled by a standard heating/stirring plate and is furnished with an exhaust port just below the bottom. This port is connected to a turnover circle driven by a hose pump. Vigorous stirring combined with circulation (1 L/min) of the reaction-suspension provides a fast and homogeneous distribution of the dissolved reactants and the suspended material. The turnover circle is furthermore armed with a 3-way port for sample collection and a measuring cell which holds a probe for continuously measuring suspension pH and temperature.

2.3. Particle coating process

The reactor system was filled with 850 ml deionised water which is then charged with 8.5 g NaN_3. The homogeneous solution was then provided with 10 g YPO_4:Bi yielding a homogeneous suspension under vigorous stirring. The suspension was then continuously stirred and pumped intensively and thereby set to a pH of 3.5–3.6 by adding some droplets of concentrated H_2SO_4. To the acidified suspension 0.66 g, 1.32 g, or 2.61 g of ($Al_2(SO_4)_3 \times 18$ H_2O was added, corresponding to the aimed 1, 2 and 4 wt% of Al_2O_3 coating relative to the used amount of YPO_4:Bi. Afterwards the dived in Hg-NIQ discharge lamp was switched on to irradiate the reaction suspension which was continuously measured for pH and temperature. The exposure was stopped after the suspension had reached a pH of 5.5–5.6. The suspension was then pumped out of the reactor and filtered afterwards. The remaining material was twice washed with deionized water and then dried at 80 °C. The dried material was kept at 200 °C over night before it was annealed at 1100 °C for 2 h.

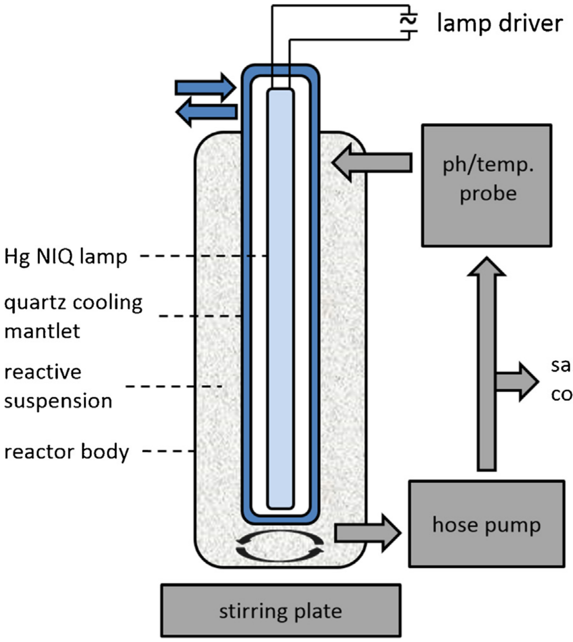

Fig. 1. Schematic UV-reactor setup.

2.4. VUV spectroscopy

The used VUV spectrometer consists of an Edinburgh Instruments FL920 spectrofluorimeter, which is equipped with a VUV excitation arm instead of the common UV/Vis excitation arrangement. The whole excitation unit is completely integrated into the FL920 spectrofluorimeter system. This VUV excitation arm consists of a D_2 discharge lamp (DS-775), an Acton Research VM-504 VUV-monochromator as well as a mirror based focusing unit. The monochromator is equipped with manually controlled micrometre-screw entrance and exit slits, as well a 1200 grooves per millimetre (g/mm) and a 2400 g/mm grating. The VUV monochromator and the whole focusing unit are evacuated by a directly flanged turbo drag pump to realize a pressure of about 3.4×10^{-5} mbar. The D_2 lamp directly irradiates into the optical path of the evacuated monochromator through an MgF_2 window. The remaining distance between the focusing unit, capped with another MgF_2 window and the sample which is placed in the unevaporated FL900 sample chamber is constantly flooded with a dry stream of N_2 to ensure VUV/UV exposure of the sample material. Sample emission is measured in a fixed 90° arrangement. The detection branch consists of a convex quartz collection lens, a Czerny-Turner Optics TMS300 monochromator equipped with a 1800 g/mm grating and a photomultiplier tube (PMT, Hamamatsu R928) running in single photon counting mode which is constantly kept at −20 °C by Peltier cooling. All measurements were conducted on thoroughly powdered samples, which were placed in circular sample holders crafted from spectralon. A correction file for the emission spectra was obtained from a tungsten incandescent lamp certified by NPL (National Physics Laboratory, UK). Emission spectra were recorded under 160 nm excitation using the 1200 g/mm grating excitation, the 1800 g/mm emission grating, excitation slit widths of 2 nm and emission slit widths of 1 nm. The measurements of excitation spectra were conducted using the 2400 g/mm excitation and 1800 g/mm emission grating, excitation slit widths of 1 nm and emission slit widths of 2 nm. The measured uncorrected excitation raw spectra were divided by the spectrum of an excitation standard sample of Sodium salicylate (NaSal) (99.5%, Merck Millipore).

2.5. Reflectance spectroscopy

Reflectance spectroscopy was performed on an Edinburgh Instruments FL920 spectrofluorimeter equipped with a custom build spectralon coated integrating sphere. Excitation was provided by a 450 W Xe arc lamp. The device is operated with two TMS300 (Czerny-Turner Optics) equipped with 1800 g/mm gratings each and a Peltier cooled (−20 °C) R928 single photon PMT (Hamamatsu). A $BaSO_4$ sample (99.99% Sigma-Aldrich) was used as reflectance standard (100%).