



Deposition of silica protected luminescent layers of Eu:GdVO₄ nanoparticles assisted by atmospheric pressure plasma jet



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ABSTRACT

Eu:GdVO₄ nanophosphors with an average size of 60 nm, synthesized by a facile solvothermal method, were deposited on monocrystalline silicon wafers by a spray-coating technique with artworks anti-counterfeiting applications in mind. Atmospheric pressure plasma jet (APPJ) was used to deposit a silica-based layer on top of the nanometric luminescent layer, in order to improve its adhesion to the substrate and to protect it from the environment. The nanophosphors were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Coating composition was investigated by Fourier transform infrared spectroscopy (FT-IR) and its morphology was characterized by scanning electron microscopy (FEG-SEM). The film thickness was evaluated by means of ellipsometry and adhesion was estimated by a peeling test. Luminescent properties of the nanophosphors deposited and fixed on silicon wafers were also measured. The whole layer resulted well-adhered to the silicon substrate, transparent and undetectable in the presence of visible light, but easily activated by UV light source.

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1. Introduction

The design and characterization of new luminescent materials (also called phosphors) have gained enormous attention in the last years due to their wide potential in an incredible range of applications, from lighting to detectors, from displays to biolabels.

In some applications they are used in the form of a powder coating, patterned or not, like in monitors and fluorescent lamps. Luminescent materials produced by conventional methods usually consist of heterogeneous particles in the micrometre range; some applications, however, take advantage of a size in the nanometre range [1], for example for biolabeling or high-resolution displays. Due to their sub-wavelength size, such luminescent particles do not diffuse visible light and may be therefore used for optically transparent coatings. Such materials may find applications in phosphor-converted LEDs, identification marker for different goods, anti-counterfeiting label for artworks or as spectral converters for solar cells.

Among them, lanthanide-based nanoparticles (Ln-NPs) constitute an important and very promising new class of nanophosphors, since they combine the interesting optical properties of the doping ions and the advantageous features of nanoparticle matrix [2]. The use of highly luminescent rare-earth doped nanoparticles is successful for a large

number of reasons, including large Stokes' shifts, long-lived excited state lifetimes (~1 ms), higher photostability and quantum yields and lower toxicity compared to organic fluorophores [3]. Moreover a large palette of colours can be easily obtained by a convenient choice of the lanthanide ions [4]. In contrast to quantum dot, the colour of the emitted light does not depend on the size of the fluorescent nanoparticles, but only on the nature of Ln³⁺ ions.

Among the different luminescent compounds, those based on Gd orthovanadate (GdVO₄) are of special interest from the optical point of view, because the indirect excitation of the doping Ln cations through an energy transfer from the vanadate anion is much more efficient than the direct excitation of the Ln electronic levels, which results in a higher luminescence [5].

Depending on the field of application, luminescent coatings of the phosphors may be obtained by different methods like gravitational settling [6,7], electrophoretic deposition [8,9], Doctor Blade [10], spray methods [11,12], sol-gel coating [13–22], screen or ink-jet printing [23], Langmuir–Blodgett technique [24] and others. Some of these methods use a binder, others a liquid media and some are dry methods. When particles are dispersed in a low-boiling liquid, once the latter has evaporated, the adhesion of the nanophosphors to the substrate is an important issue. In order to tackle this issue, particles and/or the surface substrate may be functionalised creating a chemical linkage between the coating layer and the substrate. A different physical approach is that of covering the nanoparticles with a fixation layer, which may

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also act as protecting layer. Two conditions must be satisfied for this method to be effective: a) the coating layer needs not to be compact, so as to leave islands of uncovered substrate where the fixation layer can anchor and b) the molecules of the fixation layer must be able to build a chemical link to the substrate. Thickness and homogeneity of the nanophosphors layer must be consequently taken under control. For these purposes, silica could behave as the ideal protective layer, because it has been shown to build up a transparent compact coating with a good anchorage to the substrate [25].

In the present work, a spray technique was chosen to realize a nanometric luminescent layer by depositing Eu-doped GdVO₄ nanophosphors, with a narrow size distribution in the range of 60 nm, on the surface of monocrystalline silicon wafers. Atmospheric pressure plasma jet (APPJ) was used to deposit a silica-based layer on top of the wafer for protecting the luminescent layer and improving its adhesion to the substrate, demonstrating that APPJ technology is a facile and efficient method to solve the problem of adhesion of nanoparticles deposited from a low-boiling liquid.

2. Experimental

2.1. Reagents

Gadolinium(III) nitrate hexahydrate (GdNO₃·6H₂O, Aldrich, 99.9%) and europium(III) nitrate pentahydrate (Eu(NO₃)₃·5H₂O, Aldrich, 99.9%) were selected as Ln precursors. Sodium ortho-vanadate (Na₃VO₄, Aldrich, 99.98%) was used as a vanadium source. Ethylene glycol (EG, Acros, 99+%), milliQ water and ethanol (EtOH, VWR Prolabo, 99.8%) were used as solvents. Hexamethyldisiloxane (HMDSO, Aldrich, ≥98%) was used as a chemical precursor for the APPJ silica deposition. Monocrystalline silicon wafers (Siegert Wafer GmbH, resistivity 10–20 Ω·cm, thickness 525 ± 20 μm, 2.0 × 2.5 cm) were used as substrate for the deposition and coating processes.

2.2. Preparation of Eu:GdVO₄

Nanoparticles of 5 mol% Eu-doped Gd orthovanadate were prepared according to the procedure described by Nuñez et al. [26]. Gd(III) nitrate (9.5 · 10⁻² mmol) and Eu(III) nitrate (5 · 10³ mmol) were dissolved in ethylene glycol (2.5 mL). In a separate vial, Na₃VO₄ (92.0 mg) was dissolved in an EG (1.0 mL) and milliQ H₂O (1.5 mL) mixture, then heated at around 80 °C under magnetic stirring to facilitate the dissolution of reagents. After cooling to room temperature, both solutions were mixed and the resulting solution was aged for 3 h in a tightly closed test tube at 120 °C. After ageing, the resulting dispersion was cooled down to room temperature, centrifuged to remove the supernatants and washed twice with ethanol and once with milliQ water. Finally, the precipitate was redispersed in ethanol and divided into portions to obtain different weight percentage of colloidal solutions, named Sol_{xx}, where xx stands for the weight percent of nanoparticles in ethanol (e.g. Sol25 stands for a 0.25 wt.% solution).

2.3. Nanophosphor deposition and silica coating

The Eu³⁺ doped GdVO₄ nanoparticles were deposited by spray coating, and fixed to the substrate by applying a silica-based coating by means of an atmospheric pressure plasma jet system (Openair® Plasmatreater AS400 provided by Plasmatreater GmbH).

For the spray process, the Eu-doped nanoparticles were dispersed in ethanol (with two different nanophosphor concentrations, 0.25% and 0.50%) and sonicated for 15 min; then a syringe pump pushed the ethanol solution into a coaxial nebulizer, which scanned the sample surface thanks to an x–y automatic plotter. In order to obtain a more compact and less dusty film, the silicon wafer, previously cleaned with piranha solution (H₂SO₄:H₂O₂ 7:3 vol.), was heated at about 60 °C during the deposition (see ref. [27] for a schematic representation of the apparatus).

Following preliminary tests, the operating parameters were chosen as follows: 2 mL/min (syringe flow rate), 3 bar (compressed air pressure), 10 m/min (nozzle speed) and 90 mm (nozzle height). For the number of scans used (4, 6, 8), see the discussion in Section 3.

After spray deposition, the luminescent film was encapsulated in a silica-based coating film obtained via APPJ deposition using hexamethyldisiloxane (HMDSO) as a chemical precursor. The precursor was vaporized at 125 °C and pushed towards the exit of the nozzle by means of a pressurized carrier gas. Following preliminary tests, the operating parameters were chosen as follows: 4 scans, 10 g/h (evaporator HMDSO), N₂ (ionization gas), Ar (carrier gas), 1500 m/min (nozzle speed) and 12 mm (nozzle height).

The samples without silica coating will be referred in the following as “as-deposited”, whereas the coated one will be referred as “fixed”.

2.4. Characterization techniques

X-ray diffraction pattern (XRD) of the nanoparticles was obtained using a Philips X'Pert system (Bragg–Brentano parafocusing geometry) with a nickel-filtered Cu Kα1 radiation (λ = 0.154184 nm).

Size and morphology of the nanoparticles were studied through a JEOL JEM 3010 transmission electron microscope (TEM) operating at 300 kV. The powder specimens were suspended in ethanol and sonicated; 5 μL of this suspension was deposited on a copper grid (300 mesh) coated with holey carbon film. The copper grids were allowed to dry in air.

Nanophosphors deposited on silicon wafers, both as-deposited and fixed, were analysed by a Zeiss SIGMA VP field emission gun-scanning electron microscopy (FEG-SEM), using the in-lens secondary electron (Everhart–Thornley) detector.

A Vilber Lourmat UV lamp was used on the luminescent films, both as-deposited and fixed, selecting a wavelength of 254 nm.

Photoluminescence excitation (PLE) and emission (PL) measurements were carried out using a Horiba-Jobin Yvon Fluorolog 3–21 spectrofluorimeter. A Xenon arc lamp was used as a continuous-spectrum source selecting the excitation wavelength by a double Czerny–Turner monochromator. The detection system was constituted by an iR300 single grating monochromator coupled to an R928 photomultiplier tube operating at 950 V. The excitation spectra were recorded in the 250–450 nm range with 1 nm bandpass resolution, dividing the PMT signal by the intensity of the lamp, measured by using a calibrated photodetector. On the other hand, the emission spectra were recorded in the 550–750 nm range with 1 nm band-pass resolution and corrected for the response of the instrument.

Coating thickness measurements were performed by spectroscopic ellipsometry by using a J. A. Woollam variable angle V-VASE model operating in reflection at 50° from vertical in the range 400–800 nm. The analysis of the experimental data was done by using an Effective Medium Approximation (EMA) model describing the system as a single layer combination of GdVO₄ nanocrystals and voids, with or without silica, using tabulated index of refraction. The fitting was performed by WVASE® ellipsometric analysis programme.

The fixing action of the silica-based coating layer was estimated by PL emission measurements performed before and after a Scotch™ magic tape (3M Co.) peeling test, while the scratch resistance of the fixed nanoparticles was performed using an Alpha-Step IQ surface profilometer (KLA Tencor), equipped with a contact stylus (radius of 2 μm) and applying a stylus tracking force of 2.94 mg. The scan length was 3000 μm and the speed was 50 μm/s.

3. Results and discussion

3.1. Properties of the synthesized nanophosphor particles

The X-ray diffraction pattern of the Eu³⁺ doped GdVO₄ nanophosphors here synthesized confirmed the attainment of pure

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