



Incorporation of Eu–Tb codoped nanophosphors in silica-based coatings assisted by atmospheric pressure plasma jet technology



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ABSTRACT

Different deposition methods of nanocomposite silica films with embedded $Y_2O_3:Eu^{3+}, Tb^{3+}$ by atmospheric pressure plasma jet (APPJ) technology are presented. We found that a two-step strategy consisting in the APPJ deposition of a silica film on previously deposited nanophosphors is a very efficient method to obtain nanocomposite coatings with excellent adhesion to the substrate. Moreover the APPJ deposited silica film ensures protection of the luminescent nanoparticles and preserves the photoluminescence emission properties of the nanophosphors. Optically active coatings can be therefore deposited by using this technology.

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1. Introduction

Nanostructured coatings have a wide range of industrial applications because of their mechanical and functional properties, such as abrasion resistance, UV shielding and photocatalytic effect. For example, the introduction of silica nanoparticles into the coating can improve antiscratch properties [1], while titania nanoparticles can be used for their photocatalytic effect and UV-absorbing properties [2]. Luminescent nanoparticles or nanophosphors can also provide specific optical properties. In particular, rare-earth (RE)-doped nanoparticles, because of their electronic properties arising from the 4f electrons of the dopants [3,4], have unique spectral features related to their characteristic excitation and emission properties [5]. Due to their peculiar features, the potential applications of these materials are in the fields of lighting [6], cathode ray tubes [7], plasma display panels [8], lasers [9], X-ray imaging [10], field emission displays [11], thermometry [12], security printing and anti-counterfeiting [13–15], biosensors [16–19], DNA microarrays [20–22], and emerging applications such as marker identifier for cultural heritage [23].

However, due to the sensitivity of the rare earth ions to the surrounding environment [24] and in particular to humidity [25], the possibility of encapsulating RE complexes or ions in polymeric matrices [26], inside silica nanoparticles or the realization of a silica protective

coating on the nanophosphors have been investigated [27–30]. These approaches can increase the luminescence and the quantum efficiency of the system [31,32].

Yttrium oxide (Y_2O_3) is an extensively used host material for various ions because of its low-phonon frequency, refractory properties with a melting point of 2450 °C and nontoxicity. Among the synthesis methods, the Pechini method [33] has demonstrated the capability to reliably produce monodisperse nanoparticles in a cheap and simple way [34–36].

In this work we present different approaches for the fabrication of nanostructured luminescent coatings, in which a silica matrix and RE doped Y_2O_3 nanophosphors are deposited on a surface by atmospheric pressure plasma jet (APPJ) deposition. The used rare-earths are europium and terbium. These elements have intense emissions in the visible range and due to their energy-level matching, efficient energy transfer can occur between the 5D_4 level of Tb^{3+} ions and the 5D_1 level of Eu^{3+} ions (Fig. 1).

Two different strategies to obtain luminescent coatings are compared. The first approach concerns the simultaneous deposition via APPJ system as follows: a nanoparticle aerosol is fed into the discharge zone and, simultaneously, a vapour silica precursor is fed in a different carrier channel in order to immediately fix the nanoparticles on the surface. The second strategy consists in a two-step method as follows: nanophosphors are dispersed in a liquid medium and deposited on the surface by dip-coating or by spray-coating technique. After this step, the film is encapsulated in a ceramic coating grown via APPJ atmospheric plasma deposition as described in a previous paper [37].

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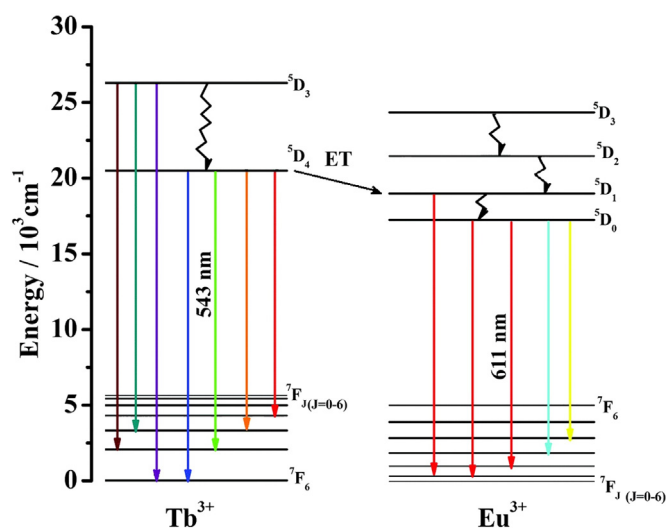


Fig. 1. Energy level scheme of Tb^{3+} and Eu^{3+} ions and indication of the energy-transfer mechanism.

The optical properties of the coatings were measured through photoluminescence (PL) excitation and emission in the visible range. Ultrasonic treatments allowed to compare the fixing capabilities of silica films while optical microscopy or scanning electron microscopy (SEM) were used to check the homogeneity of the coatings before and after ultrasonication.

2. Experimental details

2.1. Nanophosphor synthesis

Eu^{3+} and Tb^{3+} codoped Y_2O_3 nanoparticles were synthesized using the Pechini method as described in previous works [35,36]. A solution of yttrium, europium and terbium salts, solubilized with nitric acid (60%, Sigma Aldrich) and water (in proportion 1:1), citric acid (purity 99%, Sigma Aldrich) and ethylene glycol (Sigma Aldrich) was heated under stirring at 110 °C until gelation and with evolution of NO_x . After this heat treatment, the gel was annealed at 800 °C for about 2 h to allow the pyrolysis process and the formation of a crystalline powder.

The molar proportion among the total amount of the lanthanides salts, the citric acid and the glycol was 1:3:4.5. The molar proportions among the lanthanides salts were defined according to the final oxide stoichiometry and to the desired lanthanide concentrations. Nanophosphors with different optical properties were made varying the proportions among yttrium, europium and terbium. The most representative sample, in which both the europium and the terbium signals are visible, was obtained adding the same concentration (1%) of the two different rare-earths.

2.2. Nanophosphor and silica deposition

The synthesized crystalline powders were dispersed in ethanol (purity of >99.8%, Sigma Aldrich) to obtain a 1 wt.% solution and sonicated for 15 min. The substrates chosen for this work were silicon wafers which were previously cleaned with piranha solution ($H_2SO_4:H_2O_2$ 7:3).

The nanophosphors were fixed to the silicon wafers with a silica coating film obtained by atmospheric plasma deposition employing an Openair® Plasmatreater AS400 (Plasmatreat) jet system. In the nozzle a proper kilohertz excitation causes the gas ionization and the generation of the plasma into the jet at atmospheric pressure. The gas flows into the plasma generation zone where it joins the vapourized precursor and it is expelled from the discharge zone through a circular orifice on the substrate. Hexamethyldisiloxane (HMDSO, purity of >98%, Sigma Aldrich) has been used as chemical precursor for the silica deposition. It was vapourized at 125 °C and introduced at the exit of the nozzle by mean of a carrier gas.

The Eu^{3+} and Tb^{3+} codoped Y_2O_3 nanoparticles were deposited and fixed to the substrate following three different processes described in the sections that follow.

2.2.1. One-step composite preparation

This method concerned the simultaneous deposition of the doped Y_2O_3 nanoparticle dispersion and the silica coating via APPJ as follows: the nanoparticle aerosol solution was fed into the discharge zone with compressed air as carrier gas. At the same time, vapours of silica precursor were fed by a different carrier gas channel into the discharge zone. Process conditions are reported in Table 1.

2.2.2. Two-step composite preparation: dip-coating

The second method regarded a two-step process. First the doped Y_2O_3 nanoparticles were deposited on the silicon wafer by dip-coating at controlled speed of 200 mm min^{-1} and relative humidity (RH) below 20% (sample 2S_DIP). Then they were encapsulated in a ceramic coating film via APPJ deposition. The plasma process parameters are reported in Table 2.

2.2.3. Two-step composite preparation: spray-coating

The third method is also a two-step process, but the doped Y_2O_3 nanoparticle dispersion was deposited by a spray system as follows: a syringe pump pushed the solution into a nebulizer which scanned the sample surface thanks to an x–y automatic plotter. In order to obtain a more compact and less dusty film, during the deposition the silicon substrate was heated at about 200 °C.

The spray deposition parameters are reported in Table 3, while the silica coating ones are reported in Table 4.

2.2.4. Preparation of a reference film based on commercial phosphors

For comparison purposes a reference film based on commercial phosphors was prepared. Commercial phosphors with the same composition of the ones under investigation are not available. However one of the most similar commercial products that can be found in the market is PF-R7 from Risk Reactor (<http://www.riskreactor.com/>), which was studied and identified as $Y_2O_2S:Eu^{3+}$. Like most of the available commercial products, these phosphors have grain sizes in the order of 4–8 μm , therefore they cannot be applied and fixed by APPJ following the same procedures described before. A more suitable and standard deposition process which allows good homogeneity and reproducibility is bar-coating. In particular 1 wt.% PF-R7 was dispersed in a 5% solution of Paraloid B 72 (CTS) in ethyl acetate. After application on the substrate the film was dried at 90 °C in oven for 30 min.

Table 1

Process condition for one-step composite deposition on Si wafers.

Sample	Aerosol NPs (g/h)	Evaporator HMDSO (g/h)	Ionization gas	Plasma power (VA)	Nozzle speed (m/min)	Nozzle height (mm)	Treatments
1S_A	6	5	N_2	1210	5	10	6
1S_B	6	10	N_2	1210	5	10	3

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