Photoluminescence from organic–inorganic multilayers based on sol–gel derived titania

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Abstract

Transparent films of laser dye doped titania, thinner than 0.1 μm, were spin-coated from sols obtained at room-temperature from titanium tetraisopropoxide. Spectrophotometric measurements performed on the films revealed that the incorporation into the inorganic network does not affect the optical properties of the dye molecules, although the emission intensity was low, owing to the small thickness. To obtain stronger luminescence intensity avoiding the formation of cracks and defects, multilayers composed of alternated doped titania and polymethyl methacrylate thin films, were developed. Due to the refractive index contrast between the inorganic and the organic layers, the grazing-angle emission collected from the multilayers edges was found to be enhanced and considerably narrower than the single layer luminescence.

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1. Introduction

In recent years the unique optical, electrical, and structural features of materials based on titania have found several applications in a variety of fields including photonics [1–3], catalysis [4,5] and sensors development [6]. Titania can be prepared using several methods, the most common of which are chemical vapour deposition, ion sputtering, and sol–gel synthesis. In comparison with other methods, sol–gel synthesis has some advantages including low cost, low working temperature, and good control of the material properties by suitable choice of the sols composition. Furthermore, sol–gel synthesis enables the use of spin- or dip-coating techniques to obtain large area films of controlled thickness. At present, sol–gel processing is widely used to obtain passive and active media for photonics. One of the most attractive examples of that is represented by sol–gel derived titania, an optical material which is transparent in the visible range, and whose refractive index, higher than that of silica, can be tuned between 1.7 and 2.4 according
to the choice of the sol precursors, and to the kind of post-deposition thermal processing [7–9]. Such a promising material can also be doped to obtain glassy active materials, by room-temperature incorporation of small photochromic, photoluminescent, or photoconductive organic molecules into the inorganic sols. In this paper we describe a sol–gel approach used to prepare titania films doped with a laser-dye organic molecule. Iterative spin-coating of doped titania and polymethyl methacrylate (PMMA) thin films on glass substrates, enables to obtain stable and highly luminescent multilayers, whose optical properties are considerably improved if compared to those of single layers.

2. Experimental

Titania gels were obtained using titanium tetra-isopropoxide (TiPT) absolute ethanol and ethylene glycol. The dye doped sols were prepared by adding TiPT to a saturated solution of pyromethene 580 in absolute ethanol. After vigorous stirring at room-temperature, HCl 0.125 M in ethylene glycol was added drop by drop to the mixture, until a stoichiometric ratio $H_2O/TiPT = 4$ was reached. The high reactivity of titania gels, which readily form whitish microcrystals when in contact with air, complicated to a certain extent titania films deposition. To avoid that, a small amount of dimethyl formamide, used as a gelification inhibitor, was added to the sols. Uniform and transparent films of titania doped with pyromethene were obtained by depositing single drops of the precursor sols on glass substrates, and spinning at more than 4000 rpm. The thickness of the spin-coated films ranged from a few tens to about one hundred nanometers. Thicker films obtained by increasing the sols concentration or by decreasing the spinning speed, were unavoidably affected by striations and cracks induced by the coated films shrinkage during thermal densification process.

According to the literature, the refractive index of sol–gel derived titania films increases smoothly from a value of about 1.7, ascribed to thermally untreated specimens, up to a maximum value of 2.4, achievable by firing the materials at temperature as high as 800 °C [7–9]. The analysis of the red and near-infrared reflectivity interference fringes of titania films spin-coated on silicon substrates and thermally treated at 50 °C for a few minutes, reveals that the titania films developed by us have a refraction index of about 1.8 in the red.

In an attempt to increase the emitted light optical path and to maximize the luminescence intensity, we developed multilayered structures consisting of doped titania layers, alternated with PMMA layers of refractive index 1.5, spin-coated from chlorobenzene solutions of PMMA. At each deposition step the specimens were treated at 50 °C for a few minutes, and their thickness was measured by means of a step microprofilometer. Heating at 50 °C was required, as we observed that thermally untreated titania films were detached by subsequent spin-coating. The used procedure allows the stacking of stable, transparent and crack-free multilayers, consisting of several tens titania-PMMA doublets. As regards stability, we notice that aging under ambient atmosphere for several months does not affect the multilayers optical properties. Furthermore, despite the pyromethene chromophores bleach under UV irradiation, the multilayers seem to preserve their luminescence after direct exposition to continuous UV light source.

The optical quality of pyromethene doped titania films was checked by means of measurements performed in the visible range using a double beam spectrophotometer and a spectrofluorometer equipped with a 150 W Xenon lamp. A double beam spectrophotometer was used for infrared transmittance measurements, performed on thin films deposited on KBr substrates.

Grazing-angle photoluminescence measurements performed on multilayers were carried out using as excitation source a 5 mW blue LED coupled to quartz fiber with a 900 μm core. In the used experimental set-up, incidence angle was allowed to vary. Grazing luminescence was observed by using the 5× objective of an optical microscope, focused on an edge of the multilayer glass substrate. A CCD camera interfaced to the microscope was used to image and analyze the edge
grazing luminescence. The polarization state of grazing emission was investigated by interposing a linear polarizer in the light path from the multilayer to the microscope objective used to image the luminescence.

3. Results and discussion

Infrared measurements were carried out on TiO₂-based films to study the composition and chemical modification after sols deposition on substrates. Fig. 1(a) shows the infrared spectrum of the film after a few hours of thermal treatment at 150 °C. The peaks positioned at 431 and 501 cm⁻¹ are attributed to Ti–O and Ti–O–Ti stretching vibrations, and evidence the development of a titanium oxide network. No bands ascribable to titanium hydroxide are clearly observed. The weak peaks detected at 880, 1034, 1143 cm⁻¹ are assigned to the titanium ethoxide (TET) groups, grown in the sol by esterification (with ethanol) after the hydrolysis stage or by direct transesterification of TiPT precursor.

The absorption, excitation and emission spectra of an 80 nm thick film of titania doped with pyromethene and of a dilute ethanol solution of pyromethene are shown in Fig. 1(b) and (c). The position and shape of absorption and excitation peaks found in the titania film spectra, compare well with those shown in the ethanol solution spectra. As it regards the emission, environmental effects such as the observed spectral broadening and red-shift of the solid state spectrum, are consistent with those reported for dispersions of pyromethene 580 in other inorganic hosts [10]. It can be inferred that sol–gel titania is a good host for pyromethene.

The titania-PMMA multilayers irradiated by quartz fiber coupled to a blue LED exhibit a green spot in correspondence of the lighted area. The spot accounts for the luminescence isotropically emitted by the pyromethene fluorophores. Such a luminescence is unpolarized, and has a spectral shape similar to the single layer emission shown in Fig. 1(c). Whenever the multilayer thickness exceeded half one micron, intense light emissions were observed also at the multilayer edges. As an example of that, Fig. 2 shows the results of grazing photoluminescence measurements performed at the edge of a planar structure obtained by stacking ten titania-PMMA doublets, each about 200 nm
thick, on a glass substrate. The inset on the top of the figure shows the behavior of the multilayer grazing emission as the excitation incidence angle changes between $90^\circ$ and $30^\circ$. According to the results shown in Fig. 2, the grazing emission spectra are red-shifted and narrower than the luminescence of single layers, and depend on the excitation geometry. In particular, the edge emitted light reaches its intensity maximum at normal incidence, and has a minimum spectral width of about 1.5 nm, more than 40 times lower than the luminescence width of single layers. Measurements performed on thicker multilayers, obtained by stacking up to 30 titania-PMMA doublets, confirm the behavior described in Fig. 2, but for a trend shown by the grazing luminescence to shift towards the red region. As regard the emission intensity we observe that whenever the multilayer thickness was higher than about two microns, any further increase in the number of stacked layers, did not produce the expected increase of luminescence intensity, due to self-absorption. A good compromise between fluorophores concentration and self-absorption was achieved by stacking about ten couples of layers, whose ultimate thickness was in the range of two microns. The results shown in Fig. 2 can be explained in terms of a redistribution of luminescence due to the refractive index contrast in the stacking direction. In particular, the edge emission arises from a fraction of light that originates from the irradiated titania region and undergoes spatial confinement, as each doped titania layer is sandwiched between lower refraction index PMMA layers. The spatially confined luminescence is allowed to propagate through the active layer as a waveguided mode, and can be detected in correspondence of multilayer inhomogeneities, that act as scattering centres, or, as in our case, at the multilayer edges. The remarkable spectral narrowing observed in the spectra of Fig. 2 can be explained as the results of manifold interference processes suffered by light originating from each titania layer. The wave-guided character of the edge emission is confirmed.
by the sensitive intensity variations exhibited by the grazing luminescence as a function of the emission polarization angle. As an example, Fig. 3(a) and (b) display the linearly polarized grazing emission images of multilayers consisting of ten and twenty doublets, respectively. The edge luminescence of the thinner multilayer shows a high linear polarization degree and, accordingly, can be substantially eliminated acting on the polarization angle. As the thicker multilayer supports more allowed modes, the emission cannot be cancelled, but changes its spectral composition, turning from orange–yellow to green according to the polarization angle.

4. Conclusion

This work deals on a low cost approach based on sol–gel, used to develop films of titania doped with pyromethene. The results of spectrophotometric analysis suggest that the incorporation of pyromethene within inorganic titania hosts does not affect the optical properties of the dye. Iterative spin-coating followed by thermal treatment at 50 °C allows the deposition of stable and crack-free multilayers consisting of doped titania and PMMA. Owing to light confinement effects at the organic–inorganic interfaces, the multilayers luminescence is found to be stronger and narrower.

Fig. 3. Luminescence images collected at two different polarization angles from multilayers consisting of ten (a) and twenty (b) titania–PMMA doublets.
than the single layered films luminescence. On the basis of the experimental data, it should be possible to tune the multilayer grazing emission and to enhance the luminescence intensity by acting on the emitted light optical path, i.e. by choosing suitable values of the single layers thickness. Such results suggest that suitably engineered multilayers based on dye doped titania may be promising candidates as active media for photonic devices.

References