

COMMUNICATIONS

Synthesis of spherical luminescent particulate coatings

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In this communication, we show the feasibility of the pulsed laser ablation technique to make very thin, uniform luminescent coatings on particulate systems. To deposit continuous particulate coatings, the laser-induced plume from the target comes in contact with an agitated bed of core particles (size $1\ \mu\text{m}$). The pressure and nature of the background gas (inert or active) controls the cluster size of the particles in the laser plume. Experiments were conducted for laser deposition of phosphor nanoparticles on SiO_2 core particles by pulsed excimer laser (wavelength=248 nm and pulse duration=25 ns) irradiation of a yttria:Eu ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) sputtering target. © 1999 American Institute of Physics. [S0021-8979(99)04815-X]

Phosphorescent materials have significant industrial and domestic application. One of the current emerging technologies is in the area of flat-panel displays, and one of the more promising technologies is field-emission displays (FEDs). In a FED, multiple field-emission tips emit electrons which are accelerated toward a particulate-based phosphor screen which produces light. The phosphor screens are typically made from powder materials which exhibit various shape and size distributions, thus causing pixel-to-pixel nonuniformity in the screened film structure. Size and shape distributions decrease the efficiency of the flat-panel fabrication and reduce the final resolution of the flat-panel display. By synthesizing monosized, spherical phosphors, many of these problems may be reduced or eliminated.

A modified pulsed laser deposition (PLD) technique¹⁻³ was utilized to deposit phosphor coatings onto core silica particulate materials. This method is distinguished from other particulate coating techniques by its ability to make very thin, uniformly distributed, and discrete coatings in particulate systems. A laser pulse (Lambda Physik 305i, $\lambda=248\ \text{nm}$, $\tau=25\ \text{ns}$) passes through an ultraviolet transparent quartz window irradiating a phosphor target material, yttria:europium ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), creating an expanding plume of

atomic species. The laser plume is directed perpendicularly from the target material onto a mechanically agitated bed of silica powder, approximately $1\ \mu\text{m}$ in size. The typical distance between the target and the substrate is $\approx 5\ \text{cm}$. The energy densities employed in the experiments were approximately $2.0\text{--}3.5\ \text{J}/\text{cm}^2$. Coatings were conducted on $10\ \text{gm}$ samples with a laser repetition rate of $15\ \text{Hz}$ for $60\ \text{min}$ with constant agitation of the core particles. The system pressure during deposition was $200\ \text{mTorr}$ oxygen. Post processing heat treatments were conducted at $700, 800,$ and $850\ ^\circ\text{C}$ for $1\ \text{h}$ in an oxygen atmosphere to activate the phosphor layer. The thickness and surface coverage of the coating is controlled primarily by the repetition rate of the laser and the residence time of the suspension. By controlling the energy as well as the background pressure in the system, the composition and size of the clusters can be controlled. Earlier work has shown a correlation between the cluster size and the background gas pressure.⁴⁻¹¹ When the background gas pressure is increased, the cluster size changes from a few atoms to nanometer dimensions.

Figures 1(a) and 1(b) show the morphology of a continuous nanofunctionalized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor layer on $1\ \mu\text{m}$ monosized silica particles. The silica particles, prepared by sol-gel techniques are typically spherical in shape, thus leading to the spherical morphology of the nanofunctionalized particulates. The transmission electron microscope (TEM)

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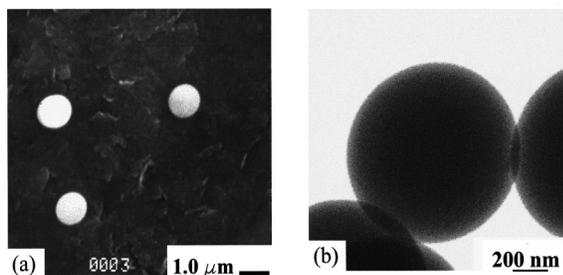


FIG. 1. (a) and (b) show the morphology of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin film on a SiO_2 particulate. It can readily be observed that the particles are geometrically spherical and $\approx 1 \mu\text{m}$ in diameter.

diffraction pattern in Fig. 2(a) and the TEM micrograph image Fig. 2(b), show two important microstructural characteristics of the nanofunctionalized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ layer, namely, (i) the layer forms a continuous film on the surface and (ii) a single-crystal-like electron diffraction pattern is obtained from the nanofunctionalized surface layer.

In $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, the Eu^{3+} ions occupy Y^{3+} lattice sites which have been shown to have either S_6 or C_2 symmetry.¹² Though the Eu^{3+} $4f-4f$ intraband transition is forbidden by the Laporte selection rule, the C_2 site does not have a center of symmetry, which results in an efficient forced transition with a peak maximum at $\sim 612 \text{ nm}$. The excited state of the forced Eu^{3+} transition is the 5D_0 state and the ground state is the 7F_2 state. The ${}^5D_0-{}^7F_2$ transitions are, typically, accom-

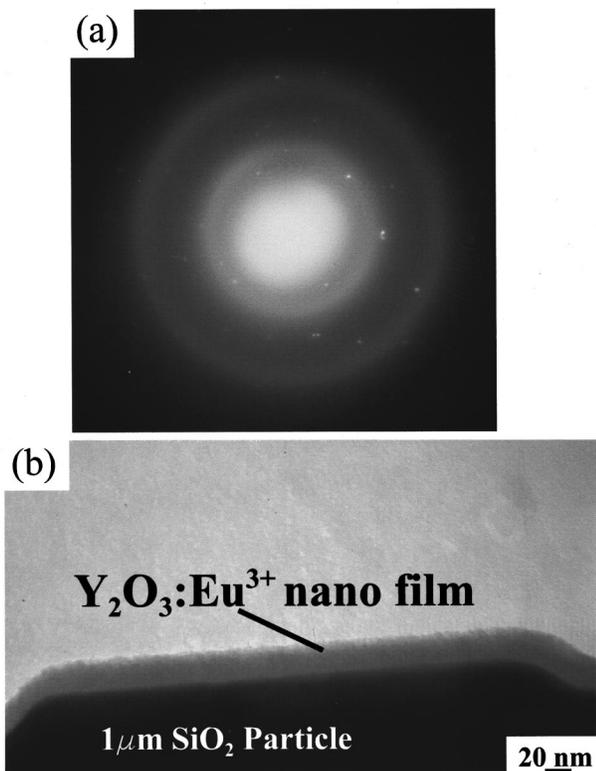


FIG. 2. The electron diffraction pattern and the bright-field image is shown in (a) and (b), respectively, showing a continuous 25-nm-thick layer on the surface. The diffraction pattern shows the amorphous rings from silica and diffraction spots from the surface layer, indication characteristics of single-crystal behavior.

PL Spectra $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ on SiO_2

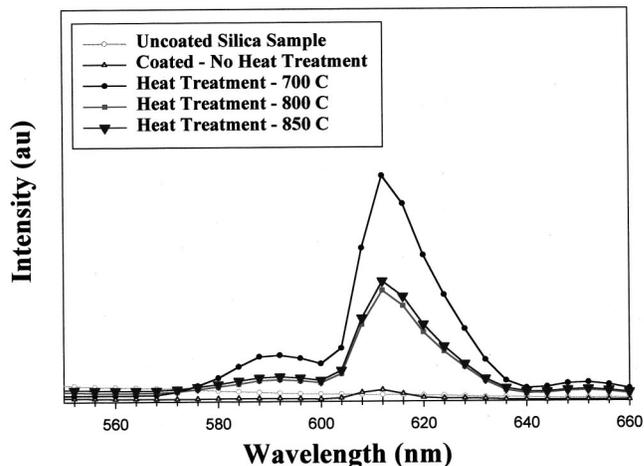


FIG. 3. The photoluminescence spectra from this nanofunctionalized particulate system for as-deposited and heat-treated samples showing emission from the ${}^5D_0-{}^7F_2$ transitions at 612 nm.

panied by less intense transitions at $\sim 590 \text{ nm}$ (${}^5D_0-{}^7F_1$) and 650 nm (${}^5D_0-{}^7F_3$). To confirm that luminescent powders were achieved, photoluminescence (PL) measurements of the $\text{SiO}_2-\text{Y}_2\text{O}_3:\text{Eu}$ powders were taken. Figure 3 shows the PL spectra for an uncoated silica sample and $\text{Y}_2\text{O}_3:\text{Eu}$ -coated powders that were heat treated at various temperatures. The emission spectra of the $\text{Y}_2\text{O}_3:\text{Eu}$ -coated powders show the typical red Eu^{3+} emission, which may suggest that the silica powders were successfully coated with $\text{Y}_2\text{O}_3:\text{Eu}$. While $\text{Y}_2\text{O}_3:\text{Eu}$ luminescence was detected for the as-deposited powder, the intensity increased with heat treatments in the range of 700–850 °C. This increased luminescence is attributed to better crystalline quality and reduced point-defect density, which are known to quench luminescence.

In conclusion, we have shown properties of nanofunctional luminescent coatings on spherical, monosized core silica particles synthesized by a pulsed laser deposition technique. The luminescent coating was shown to be $\approx 25 \text{ nm}$ thick and with a continuous architecture. Due to gas pressures used during deposition (200 mTorr), nanoparticles are formed in the gas phase and subsequently deposited on the curved silica particulate substrates. TEM diffraction patterns from the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ layer showed characteristics of single-crystalline behavior which may be due to orientation of the nanoparticle films during heat treatment. Additional studies are presently being conducted to understand the nature of layer growth on curved interfaces. The emission spectra of the $\text{Y}_2\text{O}_3:\text{Eu}$ -coated powders show the typical Eu emission at 612 nm, which suggest that the silica powders were successfully coated with $\text{Y}_2\text{O}_3:\text{Eu}$, with emission arising from ${}^5D_0-{}^7F_2$ transitions.

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