Ultraviolet free-exciton light emission in Er-passivated SnO$_2$ nanocrystals in silica

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SnO$_2$ nanocrystals are grown in silica starting from a sol-gel method and using Er doping to passivate the cluster boundaries. As a result, emission at 3.8 eV from the decay of SnO$_2$ free excitons is observed in nanostructured SnO$_2$:SiO$_2$, besides the extrinsic 2 eV luminescence of defects in SnO$_2$ and ascribable to substoichiometric nanocluster boundaries. The analysis of the extrinsic emission competitive with the ultraviolet (UV) luminescence evidences the involvement of a phonon mode at 210 cm$^{-1}$ from a SnO-like phase. The feasibility of passivated wide-band-gap nanocrystals in silica gives interesting perspectives for UV-emitting optical devices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2362583]

Wide-band-gap nanostructures are attracting considerable attention in the perspective of applications as light-emitting devices in the ultraviolet (UV) region.$^{1,2}$ Excitonic emission in nanostructured materials is the key function in that respect, together with the possibility of obtaining an optical material highly workable and compatible with the silica-based technology. In this framework, tin dioxide—with an optical gap of about 3.6 eV—is a promising system for technological application. In the case of SnO$_2$ nanoclusters in transparent silica glass has been recently proven$^3$ with interesting optical results as regards to nonlinear response,$^5$ laser photowriting,$^9$ and rare earth dispersion.$^{10-12}$ However, UV luminescence from electron-hole recombination has been observed only in crystalline SnO$_2$ bulk samples$^3$ or nanopowder colloidal suspensions.$^5$ A broad luminescence at about 2 eV is instead the only emission observed in nanostructured SnO$_2$:SiO$_2$ up to now.$^4$ As a matter of fact, the opportunity to take advantage of nanometer-size effects for a high light-emission efficiency and tunability depends on the relative rate of excitonic luminescence over all other decay paths activated in the system. Exciton self-trapping and competitive decay driven by point defects and localized states at the boundaries of the nanostructures are the main effects to be minimized for a technological application. In the case of SnO$_2$ nanocrystals in silica, a source of interphase defects is the structural mismatch arising from the different coordination features of glassy silica (SiO$_4$ tetrahedra) and rutilelike SnO$_2$ (SnO$_6$ octahedra), probably with the formation of an undercoordinated tin oxide at the nanocrystal boundaries. Indeed, suboxide boundaries have been recently identified in other nanostructured silica-based systems.$^{14}$ In these cases, the identification of the interphase and the passivation of the nanoparticle surfaces may be the key for a substantial improvement of the material.

In the present work, we give the evidence of free-exciton emission from SnO$_2$ nanocrystals embedded in a silica matrix. The result is achieved exploiting the erbium tendency of distributing at the interphase of nanostructured silica-based systems,$^{15}$ obtaining the partial passivation of the nanocrystal surfaces. The analysis of the competitive extrinsic luminescence coexisting with the exciton emission clearly identifies the involvement of an understoichiometric SnO-like phase boundary.

Optical-grade bulk samples (1 mm thick) of Er-doped silica with SnO$_2$ nanoclusters were prepared by sol-gel technique, cogelling tetraethoxysilane, dibutyl tin diacetate, and erbium nitrate with dopant concentration of 1.0 mol % erbium and 8 mol % Sn. After gelation and drying, the xerogel sample was heated (about 3 °C/h) in oxygen up to 1050 °C to induce SnO$_2$ nanoclustering and silica densification.$^{16,17}$ Nanostructure morphology was analyzed by means of transmission electron microscopy (TEM) showing SnO$_2$ nanocrystals of few nanometers in size dispersed in the amorphous silica matrix (Fig. 1). High resolution images of nanoclusters evidence single domain crystalline features with lattice parameters of the rutilelike SnO$_2$ phase. The statistical analysis of cluster sizes from several TEM images of different sample regions (inset of Fig. 1) shows a narrow distribution largely lying below the exciton Bohr radius (about 2.4 nm).$^4$

FIG. 1. TEM image of 1.0 mol % Er, 8 mol % SnO$_2$ doped silica. Inset: (right) high resolution image of a SnO$_2$ quantum dot and (left) histogram of the distribution of cluster size from TEM analysis.
Photoluminescence (PL) measurements were carried out in two excitation configurations by means of (i) the fourth harmonic of a Nd:YAG (yttrium aluminum garnet) laser to excite at 4.7 eV within the SnO$_2$ band-to-band transition energy range and (ii) the third harmonic of a Nd:YAG laser to excite at 3.5 eV in the low-energy SnO$_2$ absorption tail caused by localized and defect states in the nanoparticle interphase. In the first configuration, UV and visible luminescence were dispersed by a single grating monochromator with 1.5 nm bandwidth and detected by a photomultiplier tube; in the second configuration, the emission signal was detected by a charge-coupled device camera coupled with a polychromator with 1.5 nm bandwidth. All measurements were corrected for the overall spectral response. Raman spectra were obtained at 300 K in backscattering configuration by means of an Ar$^+$ laser at 488 nm with a resolution of about 1 cm$^{-1}$.

Figure 2 shows the PL spectrum excited at 4.7 eV. The outstanding feature in the spectrum is the UV emission centered at 3.9 eV, just as it is expected for the radiative recombination of electron-hole pairs confined in SnO$_2$ nanocrystals with 2 nm average radius, according to data in inset of Fig. 1. In fact, from the values of nanocrystal radius $R$ and exciton reduced mass $m^*$ (about 0.27$m_e$ in SnO$_2$), the energy shift $\Delta E$ of the exciton recombination energy with respect to the bulk gap energy (3.6 eV) is $\Delta E = (\hbar^2/2m^*)/(\pi^2/R^2) \approx 0.3$ eV. The 3.9 eV emission, never observed in undoped samples, is thus the evidence of free-exciton decay in tin dioxide nanocrystals embedded in silica. The present data do not allow to give a reliable estimation of the conversion efficiency. Anyway, this result suggests that erbium ions might play a passivating function on the defects responsible for the exciton trapping.

Nevertheless, below 2.5 eV, the spectrum in Fig. 2 also shows the broad PL band from exciton trapping and decay in localized states, with the superposition of narrow peaks from erbium transitions $^5S_{3/2} \rightarrow ^1I_{15/2}$ at 2.25 eV and $^4F_{9/2} \rightarrow ^1I_{15/2}$ and $^2H_{11/2} \rightarrow ^1I_{15/2}$ at 1.9 and 2.38 eV, respectively. A weak emission band at 3.1 eV is ascribable to Sn-related oxygen vacancies in the silica matrix ($\beta$ band), as expected from the dispersion of a small fraction of Sn atoms from SnO$_2$ nanocrystals to silica during UV laser excitation.

The presence of the defect-related PL component indicates that the passivation is incomplete. To identify the origin of the competitive decay process, the extrinsic PL band has been analyzed as a function of the temperature, evidencing the coupling with a specific phonon mode of the responsible phase. PL spectra excited at 3.5 eV at increasing temperature from 80 to 290 K are reported in Fig. 3. The broad band of defectlike luminescence dominates the spectra and it is accompanied by a series of positive and negative narrow components due to absorption and emission at the erbium transitions. The defect-related PL band shows a broadening and a shift to higher energies with increasing temperature. Information on the decay dynamics may be extracted from the analysis of the energy moments of the emission band fitted by a Gaussian band. The energy moments $M_0$, $M_1$, and $M_2$ of the spectral distribution $f(E)$ of PL intensity are obtained, respectively, by calculating $\int f(E)dE$ (integrated intensity), $(1/M_0)\int Ef(E)dE$ (spectral position), and $(1/M_0)\int E^2f(E)dE-M_1$ (energy bandwidth).

The normalized zeroth moment $M_0$ in inset of Fig. 3 (filled circles) follows the expected temperature dependence, with a decrease of luminescence efficiency at growing temperature due to the activation of nonradiative decay channels. A blue shift of the PL band is evidenced by $M_1$ values (open circles). The thermal behavior of the second spectral moment $M_2$ may be analyzed in the approximation of broadening dominated by electron-phonon coupling. In this case, the total PL bandwidth is given by the following equation:

$$M_2 = A(h\omega_{\text{ph}})^2 \coth \left(\frac{h\omega_{\text{ph}}}{2k_B T}\right) + \sigma_{\text{inh}}^2,$$

where $k_B$ is the Boltzmann constant, $h\omega_{\text{ph}}$ is the mean energy of the local mode coupled with the electronic transition, $A$ the number and the linear coupling constant of vibrational modes in Einstein’s oscillator model, and $\sigma_{\text{inh}}$ accounts for the temperature independent inhomogeneous broadening due to site-to-site disorder at the cluster boundaries. Looking at Eq. (1), the analysis of $M_2$ may give an indication of the phonon mode involved in the decay process. Figure 4 shows $M_2$ as a function of the temperature, together with the fit to Eq. (1). The resulting phonon energy $h\omega_{\text{ph}}$ is about 200 cm$^{-1}$, consistent with the $A_{1g}$ mode of tin monoxide at 211 cm$^{-1}$. Raman spectra on the same sample confirm the presence of a vibrational peak at 210 cm$^{-1}$ (inset of Fig. 4). These evidences concur in identifying a SnO-like phase.
ordination shell. These results clarify the decay mechanism of the silica-nanocrystal interface, probably thanks to the bonding properties of Er doping. It suggests that Er doping succeeds in passivating part of the nanocrystal surface, probably localized at the silica-nanocrystal interface.

In summary, the results on the one hand indicate that a SnO phase plays a role in the compensation of the structural mismatch at the nanocrystal surface, probably due to the detection of free-exciton luminescence, which is also shown as a schematic of the $A_{1g}$ phonon mode in SnO. On the other hand, the detection of free-exciton luminescence suggests that Er doping succeeds in passivating part of the nanocrystal surface, probably thanks to the bonding properties of rare earth ions accommodating several kinds of oxygen coordination shell. These results clarify the decay mechanisms of the system and open the way to an improvement of the passivation strategy and UV emission efficiency.

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