

Erbium-implanted silica colloids with 80% luminescence quantum efficiency

L. H. Slooff, M. J. A. de Dood, A. van Blaaderen, and A. Polman

FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

(Received 6 March 2000; accepted for publication 24 April 2000)

Silica colloids with a diameter of 240–360 nm, grown by wet chemical synthesis using ethanol, ammonia, water, and tetraethoxysilane, were implanted with 350 keV Er ions, to peak concentrations of 0.2–1.1 at. % and put onto a silicon or glass substrate. After annealing at 700–900 °C the colloids show clear room-temperature photoluminescence at 1.53 μm , with lifetimes as high as 17 ms. By comparing data of different Er concentrations, the purely radiative lifetime is estimated to be 20–22 ms, indicating a high quantum efficiency of about 80%. This high quantum efficiency indicates that, after annealing, the silica colloids are almost free of OH impurities. Spinning a layer of polymethylmethacrylate over the silica spheres results in an optically transparent nanocomposite layer, that can be used as a planar optical waveguide amplifier at 1.5 μm that is fully compatible with polymer technology. © 2000 American Institute of Physics.
[S0003-6951(00)00425-3]

Integrated optics is becoming increasingly important in modern telecommunication technology. One important field of research is the study of rare-earth doped solid state planar optical amplifiers. Rare earth ions show sharp absorption and emission bands and relatively long luminescence lifetimes. Particularly the rare earth ion erbium (Er) is of interest due to its intra $4f$ -transition from the first excited state to the ground state around 1.53 μm ($^4I_{13/2} \rightarrow ^4I_{15/2}$), which is one of the standard telecommunication wavelengths. Planar amplifiers have been realized based on rare earth doped silica, Al_2O_3 , phosphate glasses, and LiNbO_3 .^{1,2}

Because of the increasing importance of polymer optical technology it would be interesting to fabricate Er-doped polymer waveguides, for application in lasers and amplifiers operating at 1.5 μm . Previously, we and others have investigated organic rare earth complexes which can be dissolved in a polymer matrix.^{3–5} Most of these complexes contain C–H bonds of which the second vibrational overtone can quench the rare earth luminescence.^{6,7} Therefore an alternative approach to encapsulate Er in a polymer is desired. It is well known that silica is an excellent host for rare earth ions yielding long luminescent lifetimes.^{8,9} It would therefore be interesting to study if the material properties of polymers (easy processing) could be combined with the properties of silica (long Er luminescence lifetime). In this letter we study the optical doping of colloidal silica particles with Er using ion implantation. The influence of Er concentration and anneal temperature on the luminescence intensity and lifetime is determined. It is found that the silica colloids are an excellent host for Er, yielding a quantum efficiency as high as 80%. As a first demonstration of the possible application in polymer waveguides, optical transmission measurements are shown for a polymer film doped with these Er-doped silica colloids.

Silica colloids with a diameter of 240 or 360 nm were synthesized as described by van Blaaderen *et al.*¹⁰ Solutions of 10 ml ethanol, 0.7 ml NH_3 (28 wt. % in water), 0.8 ml H_2O , and 0.4 ml tetraethoxysilane (TEOS, 99%) were

mixed and stirred for 1 h at room temperature, resulting in the nucleation and growth of silica colloids with a diameter of 244 ± 10 nm, as measured using scanning electron microscopy (SEM). In one set of samples, the diameter of the spheres was increased to 360 nm by subsequent addition of TEOS to the reaction vessel.¹¹ After the reaction, the suspension was centrifuged and the remaining colloids were dissolved in pure ethanol. Droplets of the solution were then put onto a silicon substrate or a microscope cover glass (cleaned with a 1 M KOH/ethanol solution). After evaporation of the ethanol, a thin layer of colloids remained. Next, the samples were irradiated with 350 keV Er ions at various fluences ranging from 0.9×10^{15} to 5.5×10^{15} ions/cm². The projected range of 350 keV Er in silica is 160 nm. Implantation of these ion fluences into a planar film would result in a Gaussian Er distribution with a full width at half maximum (FWHM) of 34 nm. It is obvious that in these nonuniform, colloidal layers a less well-defined concentration profile builds up. After implantation the samples were annealed in vacuum at 100 °C for 1 h and then for another hour at different temperatures in the range 700–1000 °C.

In order to study the Er incorporation in the colloids, Rutherford backscattering spectroscopy (RBS) measurements were performed, using a 2 MeV He^+ beam at a scattering angle of 165°. Scanning electron microscopy (SEM) was performed at an electron energy of 10 keV. Photoluminescence (PL) measurements were performed using the 488 and 515 nm lines of an Ar ion pump laser at a power density of 50–60 mW/mm² for excitation. The laser beam was modulated with an acousto-optic modulator. The PL signal was focused into a 48 cm monochromator and detected with a liquid-nitrogen-cooled Ge detector, using standard lock-in techniques, yielding a spectral resolution of 6 nm. Lifetime measurements were performed by monitoring the decay of the luminescence after switching off the light source. A digitizing oscilloscope was used to average the decay curves. Optical transmission measurements were performed at nor-

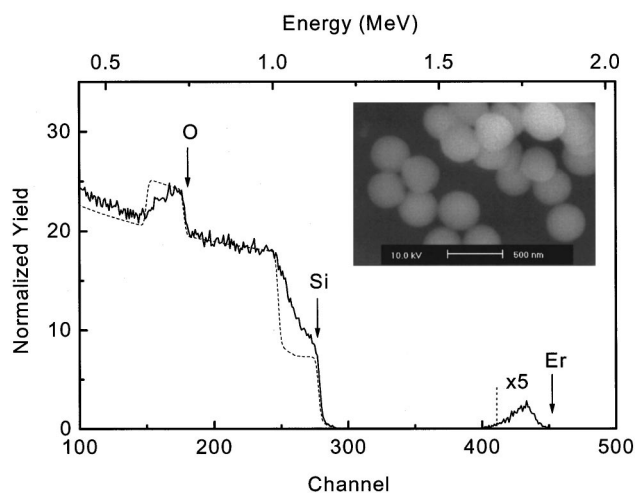


FIG. 1. RBS spectrum of a single layer of Er-implanted (350 keV, 9×10^{14} Er/cm²) silica colloids on a Si substrate (solid line). A 2 MeV He beam was used at a scattering angle of 165°. A simulation of a 360 nm SiO₂ film on a silicon substrate (dashed line) is shown for comparison. The dashed line at channel 410 indicates the position of the SiO₂/Si interface for Er. The inset shows a SEM image of the same sample.

mal incidence using a spectrometer at wavelengths ranging from 300 to 1700 nm.

Figure 1 shows an RBS spectrum of a Si sample covered with a single layer of 360 nm diameter colloids, implanted with 9×10^{14} Er/cm². For reference, a simulation for a 360 nm pure SiO₂ layer on a Si substrate is shown (dashed line). The surface channels of Er, Si, and O are indicated by the arrows. The Si content at the surface is almost similar to the Si content in pure SiO₂, indicating that the substrate is almost completely covered with colloids. The Si yield then increases with decreasing energy, as a result of the spherical shape of the colloids. The Si yield coincides with that of the simulation at channel 245, consistent with the colloid diameter of 360 nm. The signal between channel 400 and 500 is due to the implanted Er. The peak concentration is 0.18 at. %. Note that a small fraction of the implanted Er has entered the Si substrate, as is evident from the Er tail near channel 400. The inset in Fig. 1 shows a SEM image of the deposited colloids (360 nm diameter), showing a rather unordered array of particles extending over several layers.

The samples used for PL measurements consisted of about 3–4 layers of silica colloids, as determined from RBS simulations and SEM. Figure 2 shows the PL spectrum of colloidal silica particles implanted to a peak concentration of 1.1 at. % and annealed at 950 °C for 1 h. The implantation and annealing caused no deformation of the silica spheres. The spectrum shows typical Er³⁺ luminescence around 1.53 μm due to transitions from the ⁴I_{13/2} to the ⁴I_{15/2} level. The two peaks result from Stark splitting of the Er³⁺ levels and are characteristic for Er³⁺ in SiO₂.¹ The width (32 nm FWHM) is due to the thermal distribution over the Stark levels and homogeneous and inhomogeneous broadening. It is difficult to compare PL intensities for different implanted samples as the colloid coverage varies from sample to sample, and because of the fact that the pump beam is strongly scattered by the silica spheres, which results in non-uniform pumping. However, on average the intensity in-

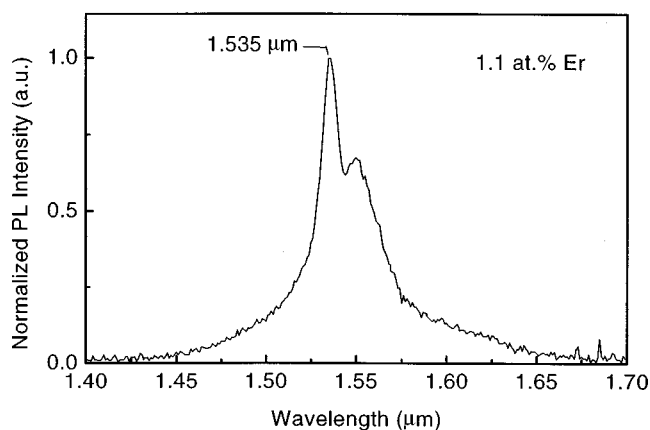


FIG. 2. Photoluminescence spectrum for a thick layer of colloids, implanted with Er (1.1 at. %), taken using 515 nm pump light at a power of 60 mW/mm².

creases for increasing doping concentration up to at least 1.1 at. %.

Figure 3(a) shows the peak PL intensity of samples implanted with 0.2 at. % Er, annealed at various temperatures for 1 h. Below 700 °C, no measurable PL was observed. This might be due to water that is physisorbed on the surface or trapped in the pores of the silica matrix. Water is known to quench the Er³⁺ luminescence, as the first overtone of the O–H vibration ($E_0 = 3400$ cm⁻¹) is strongly resonant with the Er³⁺ transition ($E = 6500$ cm⁻¹). Indeed, work by Fan *et al.*¹² and Tien and Chau¹³ on bulk silica samples, grown in a similar way as the colloids, shows that between room temperature and 200 °C, weakly bound water and residual organic molecules vaporize, followed by the removal of chemically bound molecular water between 300 and 800 °C. Figure 3(a) shows a large scatter in the data above 700 °C, but the general trend is a decrease in PL intensity, certainly for tem-

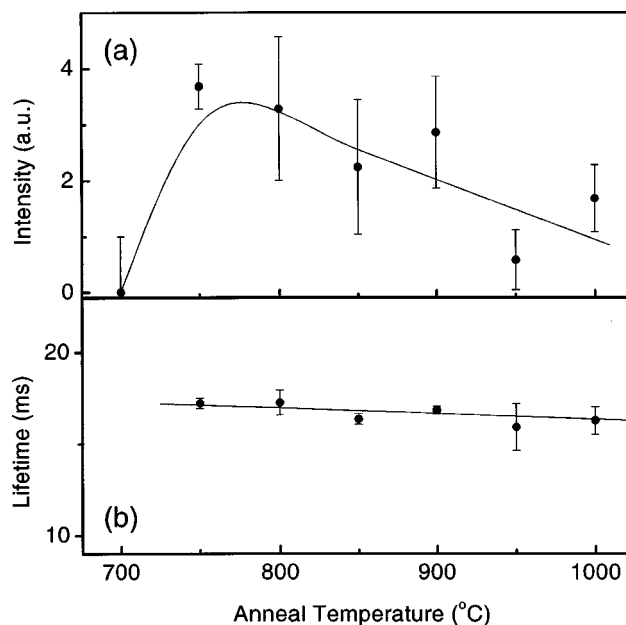


FIG. 3. (a) Average peak photoluminescence intensity at 1.535 μm as a function of anneal temperature for Er-implanted silica spheres (0.2 at. %). Pump wavelength 488 nm, pump power 50 mW. The large error bars are due to the large variation in colloid coverage over the surface. (b) Luminescence lifetime of Er-implanted silica spheres (0.2 at. %) as a function of anneal temperature.

peratures above 900 °C. This may be due to the precipitation of Er, as has been observed before in Er implanted SiO₂.⁸ Figure 3(b) shows luminescence lifetime measurements as a function of anneal temperature for an Er³⁺ concentration of 0.2 at. %. For anneal temperatures below 700 °C the PL intensity was too low to perform lifetime measurements. The lifetime for anneal temperatures between 750 and 1000 °C is about 17 ms and is almost independent of anneal temperature. We have also performed lifetime measurements for samples implanted at higher doses, and found that increasing the Er concentration from 0.2 to 1.1 at. % results in a decrease in the luminescence lifetime from 17 to 10 ms. These lifetimes are among the highest observed in silica glass. Assuming that the decrease in lifetime is due to concentration quenching, we can estimate the radiative lifetime by linearly extrapolating to zero Er concentration and find $\tau_{\text{rad}}=20\text{--}22\text{ ms}$.¹⁴ The long lifetimes observed in this work show that the silica glass made by wet chemical synthesis is an excellent host for Er. It indicates that the water impurity content in this glass after annealing is very small (<1 ppm).¹⁴ We note that the long radiative lifetime can be partly attributed to the fact that the Er-implanted colloids are partly surrounded by air, causing the local optical density of states in the colloids to be lower than that of bulk SiO₂.^{15,16} To test this idea, we have deposited 0.2 at. % Er-implanted colloids on a Si substrate ($n=3.45$). Indeed, they show a reduced luminescence lifetime of about 12 ms.

Two months after the first PL measurements on the Er-implanted colloidal particles, we performed the same measurements again and found that the luminescence intensity and lifetime were strongly reduced. After annealing at 475 °C, both the luminescence intensity and lifetime returned to the level observed after the initial anneal. This suggests that some time after the anneal, a thin film of water covers the colloids, which makes it necessary to coat the silica spheres with a protective layer, e.g., a polymer.

In order to investigate the application of these colloids in polymer waveguides, undoped silica colloids with a diameter of 244 nm were deposited onto a microscope cover glass. Next, the samples were annealed for one hour at 100 °C, and subsequently a solution of 1.5 g polymethylmethacrylate (PMMA) in 10 ml chloroform was spun onto the substrate at a spin rate of 2000 rpm for 30 s, resulting in 1- μm -thick films. An optical transmission measurement on this colloid/polymer nanocomposite film is shown in Fig. 4. For reference a spectrum of the glass substrate is shown (solid line), together with the transmission spectrum of the substrate covered with silica spheres (without polymer, dashed line). As can be seen, without the polymer coating, the transmission at short wavelengths is strongly reduced due to scattering by the silica spheres. Covering the spheres ($n=1.45$) with a PMMA ($n=1.48$) layer reduces the scattering by reducing the refractive index difference between the SiO₂ colloids and its surroundings. Note that in this measurement the interaction length is only 1 μm . In a homogeneously doped polymer

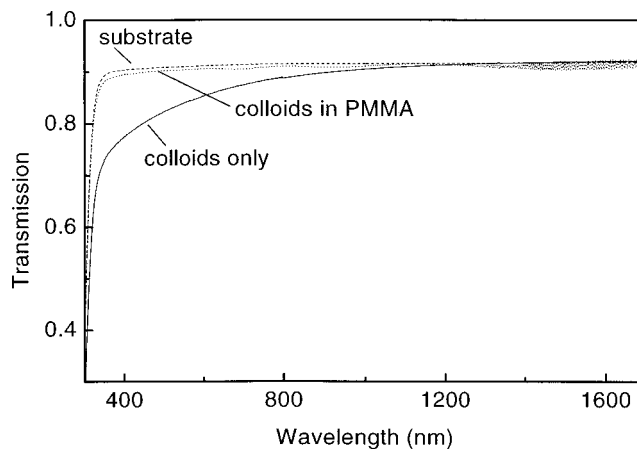


FIG. 4. Optical transmission measurements of a 1 μm silica/polymer nanocomposite film on a microscope cover glass (dotted line) and of a cover glass with colloids only (dashed line). Measurements are also shown for a bare cover glass (solid line).

waveguide with a length of a few cm, the scattering would be too high and smaller particles or a polymer with a refractive index of 1.45 are needed to eliminate the scattering losses. Such polymers are readily available.

In conclusion, we have observed room-temperature luminescence at 1.5 μm from Er-implanted silica colloidal spheres. The luminescence lifetime of Er is about 17 ms, and the quantum efficiency 80%. Thermal annealing at 750 °C is required to optimize the PL. The colloids can be embedded in a polymer to achieve an optically active nanocomposite waveguide layer.

This work is part of the research program of the FOM and was financially supported by NWO and the SCOOP program of the European Union. Dirk Vossen is gratefully acknowledged for preparing the silica colloids and Carlos van Kats and Teun van Dillen for help with the SEM measurements.

¹A. Polman, *J. Appl. Phys.* **82**, 1 (1997).

²P. G. Kik and A. Polman, *MRS Bull.* **23**, 48 (1998).

³S. Lin, J. Feuerstein, and A. R. Mickelson, *J. Appl. Phys.* **79**, 2868 (1996).

⁴L. H. Slooff, A. Polman, M. P. Oude Wolbers, F. C. J. M. van Veggel, D. N. Reinhoudt, and J. W. Hofstra, *J. Appl. Phys.* **83**, 497 (1998).

⁵L. H. Slooff, A. Polman, S. I. Klink, G. A. Hebbink, L. Grave, F. C. J. M. van Veggel, D. N. Reinhoudt, and J. W. Hofstra, *J. Opt. Mater.* **14**, 101 (2000).

⁶G. Stein and E. Würzberg, *J. Chem. Phys.* **62**, 208 (1975).

⁷V. L. Ermolaev and E. B. Sveshnikova, *Russ. Chem. Rev.* **63**, 905 (1994).

⁸A. Polman, D. C. Jacobson, D. J. Eaglesham, R. C. Kistler, and J. M. Poate, *J. Appl. Phys.* **70**, 3778 (1991).

⁹W. J. Miniscalco, *J. Lightwave Technol.* **9**, 234 (1991).

¹⁰A. van Blaaderen and A. Vrij, *Langmuir* **8**, 2921 (1993).

¹¹D. L. J. Vossen, M. J. A. de Dood, T. van Dillen, T. Zijlstra, E. van der Drift, A. Polman, and A. van Blaaderen (unpublished).

¹²X. Fan, M. Wang, and G. Xiong, *Mater. Sci. Eng., B* **21**, 55 (1993).

¹³P. Tien and L.-K. Chau, *Chem. Mater.* **11**, 2141 (1999).

¹⁴E. Snoeks, P. G. Kik, and A. Polman, *Opt. Mater.* **5**, 159 (1996).

¹⁵E. Snoeks, A. Lagendijk, and A. Polman, *Phys. Rev. Lett.* **74**, 2459 (1995).

¹⁶W. Barnes, *J. Mod. Opt.* **45**, 661 (1998).