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Silicon nanoclusters containing nitrogen and sensitization of erbium luminescence in SiO_x:Er

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Abstract

Silicon-rich silica samples doped with erbium were grown by PECVD and characterized by photoluminescence, time-resolved photoluminescence and Fourier transform infrared spectroscopy. We observe that upon increased silicon content, the absorption spectrum reveals the formation of a Si–N bond. This indicates the possible incorporation of nitrogen from the precursor N_2O gas into the Si nanoclusters. The highest erbium photoluminescence is obtained for the sample with the highest silicon content and its decay characteristics are nearly single exponential with a time constant of 5 ms. In addition to erbium emission, a visible luminescence peak at about 550 nm is observed. This shows multi-exponential decay kinetics with decay times of the order of 10 ns. We propose that this emission is due to small Si nanoclusters covered by a Si–N shell. From the measurements, we study a mechanism to explain the erbium excitation in this material.

Keywords: Photoluminescence; Si nanoclusters; Erbium

1. Introduction

Recently, silica doped with erbium and silicon nanoclusters has been studied extensively. The erbium emission at 1.54 μm is important from the point of view of optoelectronic applications as it matches the minimum loss in silica fibers [1]. However, in pure silica only resonant excitation is allowed, with a very small excitation cross-section of the order of 10^{-21} cm^2 [2]. A more efficient excitation path is present in silica doped with erbium and Si nanoclusters. The nanoclusters act as sensitizers of erbium luminescence allowing broad band excitation at wavelengths not absorbed by erbium, with an effective excitation cross-section of about $\sim 10^{-16}$ cm^2 [3,4]. Electrical excitation of erbium has also been reported for this material [5]. Since it was found that only small fraction of erbium ions can be excited via Si nanoclusters [6], current research is focused on optimization of this material and understanding the sensitization mechanism. In this paper, we present a study of a set of SiO_x:Er samples with different silicon excess annealed at different temperatures. In contrast to other studies of the optical properties of this material, our samples show bright visible photoluminescence (PL) in addition to that from erbium at 1.54 μm. We discuss the visible PL and relate this to the presence of nitrogen, which is incorporated into this material during the growth.

2. Experimental

The SiO_x:Er layers of thickness about 1 μm were deposited on Si substrates by plasma enhanced chemical vapour deposition (PECVD). Silane (SiH_4) and nitrous oxide (N_2O) were used as precursor gases—the former being diluted to 5% in argon, and erbium $(thd)_3$ vapour with argon as a carrier gas was used to achieve erbium doping during the growth. The fluence of silane was varied to obtain samples with different silicon excess. The following values of silane fluence were used: 5 sccm (set of samples o4), 7.5 sccm (samples o2), 10 sccm (samples o3) and 12.5 sccm (samples o5). Note that these values are the values of silane fluence, not of the combined silane/argon flow, i.e. they have been corrected by the dilution factor. After deposition the samples were annealed to precipitate and grow Si nanoclus-

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ters. For each set of samples different annealing temperatures were used, ranging from 800 to 1150 °C. The erbium photoluminescence was excited using an Ar^+ laser at a wavelength of $\lambda_{exc} = 476$ nm (i.e. non-resonant with Er absorption lines), analyzed with a Bentham M300 single grating monochromator, and detected with an InGaAs photodiode. To measure time-resolved erbium PL, the laser was modulated with Pockels cell, and waveforms were recorded with a digital oscilloscope. The time resolution of the system was of the order of 50 μs. In the visible spectral range, photoluminescence spectra and decay traces were measured with Edinburgh Instruments Time Correlated Single Photon Counting System with pulsed laser diode operating at $\lambda_{exc} = 405$ nm as an excitation source. The infrared absorption spectra were measured by a Perkin-Elmer Spectrum ONE FTIR spectrometer with a resolution of 4 cm^{-1}.

3. Results and discussion

Fig. 1 presents spectra of erbium PL. The highest erbium emission is obtained for sample with the highest silicon content. This, along with transmission electron microscopy (TEM) studies of similar material grown using the same deposition conditions, indicates the presence of silicon nanoclusters, which are needed to allow indirect excitation. In the inset the decay trace of erbium PL for this sample is presented. The straight line is a single exponential fit with the value of decay time $\tau \approx 5$ ms. A slightly better fit can be obtained with a stretched exponential function $\exp(-(t/\tau)^{\beta})$, which gives the same value of the decay time and $\beta \approx 0.9$. This value of β means that decay trace can be reasonably well approximated with a single exponential function, which suggests that, within the time resolution of our measurements, processes, such as backtransfer and upconversion may be neglected in this sample. The lifetime of erbium photoluminescence is relatively long, as values of about 3 ms are usually reported for this material [3].

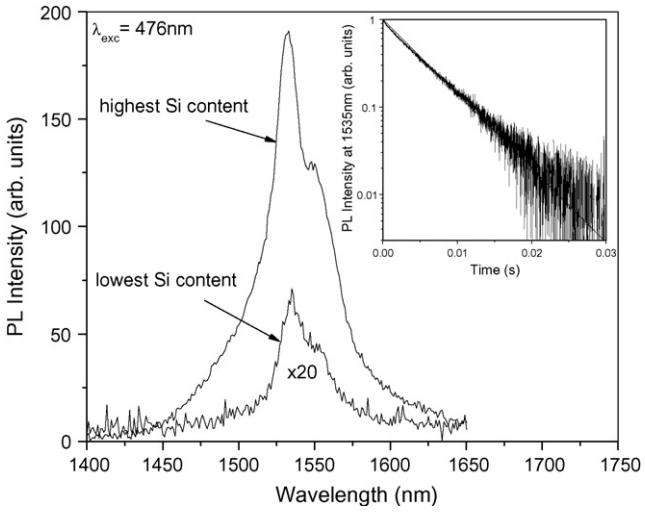

Fig. 1. Photoluminescence spectra in the region of erbium emission for samples with highest silicon content (silane flow during deposition: 12.5 sccm) and lowest silicon content (silane flow during deposition: 5 sccm). Both samples were annealed at 1000 °C. The *inset* shows the decay trace of erbium photoluminescence at 1535 nm for the sample with the highest Si content.

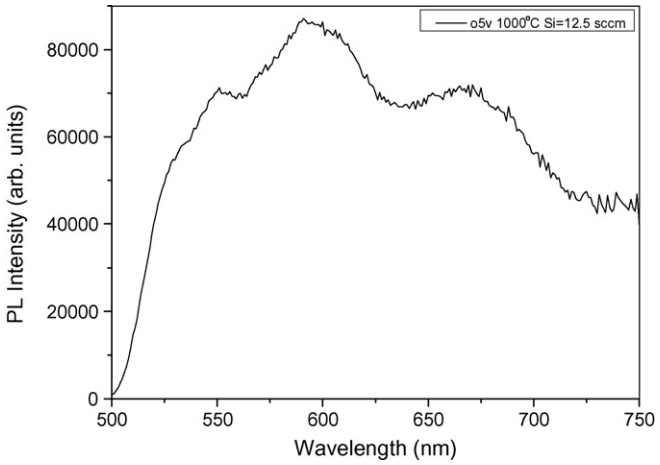

Fig. 2. Photoluminescence spectrum in the visible range for sample o5v annealed at 1000 °C.

In addition to erbium photoluminescence we can observe intense visible emission, as presented in Fig. 2. The spectra of visible photoluminescence are very similar for all samples studied, i.e. broad and irregular, with several peaks superimposed on a broad feature. This spectral shape is probably a result of thin film interference. The short-wavelength edge is due to a long-pass filter used to eliminate the light of the excitation source. Similar visible photoluminescence in this material was also reported by other authors [7,8].

The decay of the visible photoluminescence is multi-exponential with a very short decay time of the order of nanoseconds. Fig. 3 presents decay traces of visible PL measured at 550 nm for a set of samples of different Si content annealed at 800 °C. The stretched exponential function is not the best fit for these decay curves. Instead, a multi-exponential function has to be used, with up to five exponential components with decay times ranging from 0.3 to 10 ns. For three of the samples it can be observed that the decay becomes longer when the silicon content is increased. However, for the sample with the lowest Si content the decay is also relatively long.

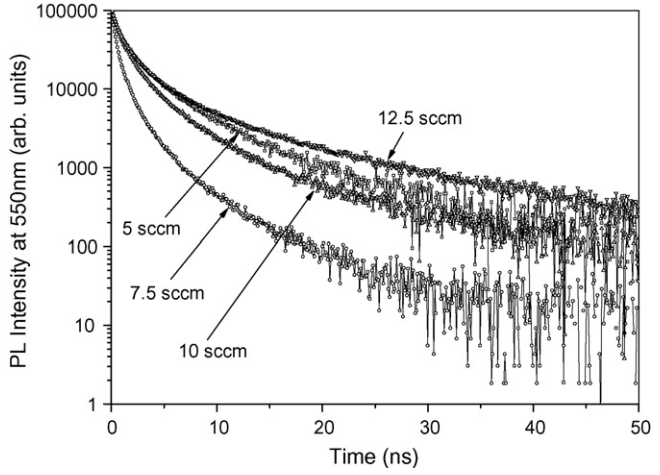

Fig. 3. Decay traces of visible PL measured at 550 nm for samples annealed at 800 °C. The samples have different silicon content due to different values of silane flow used during the deposition, as indicated.