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Features of Er^{3+} luminescence in fluorine-doped amorphous silicon dioxide fabricated by low-temperature plasma CVD

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Abstract

Spectra and photoluminescence kinetics of Er^{3+} ions incorporated in an amorphous host of fluorine-doped silicon dioxide synthesized by surface plasma chemical vapor deposition (SPCVD) are investigated at temperatures of 27–300 K. Luminescence is excited with an Ar^{+} laser at a wavelength of 514.5 nm and with a diode laser at a wavelength of 975 nm. Narrow and well-defined components of Stark manifolds with a small contribution from inhomogeneous broadening intrinsic to Er^{3+} ions in crystalline, but not amorphous, hosts are revealed and identified in photoluminescence spectra. The structure of the Stark manifolds is well-resolved at low temperatures. The presence of the well-resolved Stark structure in the spectra is indicative of stable anion complexes formating the Er^{3+} local neighborhood presumably associated with fluorine incorporation. This neighborhood is formed during the low temperature plasma chemical synthesis and is destroyed upon glass fusion.

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1. Introduction

Plasma chemical synthesis of silicon dioxide by means of a reduced-pressure microwave-induced discharge leads to the formation of various structurally non-equilibrium composites of a high optical quality [1]. It is shown in particular, that the plasma chemical deposition can yield amorphous silicates doped by a high concentration of erbium, in which Er^{3+} ions are homogeneously brought into glass matrix [2,3]. In the absence of conditions for erbium clustering, which significantly enhance concentration quenching, quantum efficiency of luminescence excitation of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ laser transition in Er^{3+} ions may be high, thus distinguishing these glasses from their fused counterparts. This feature opens a way for the application of non-fused amorphous silicates in integrated optics as media for waveguide lasers and amplifiers, where high quantum gain efficiency together with a high concentration of an activator is demanded [4]. Such lasers and amplifiers are a topical issue especially for the 1550 nm wavelengths region of the telecom band.

In fused silicate glasses even at a moderate erbium concentration, when no explicit clusters formation leading to oxides decomposition into separate immiscible phases occurs, there is a significant decay in luminescence quantum efficiency of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ laser transition brought about by the up-conversion effect. The effect is caused by a pair interaction between closely located in the host Er^{3+} ions simultaneously excited in $^4I_{13/2}$ state leading to the

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non-radiative relaxation of one of them in $^4I_{15/2}$ ground state and the excitation of the other in higher energetically located $^4I_{11/2}$ state [5].

High quantum excitation efficiency of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ laser transition in Er^{3+} ions incorporated into non-fused amorphous silicates results from peculiarities of material deposition by the plasma chemical technology. It is the use of this technology that prevents erbium clusters formation caused by a low mutual solubility of erbium and silicon oxides in melts. Damping of clusters formation in the process of low temperature plasma chemical synthesis occurs owing to a statistically uniform flow of glass forming species, which reaches a relatively cold substrate from the gas phase in conditions when the species (especially erbium) cannot migrate in the volume. Such glasses can be specified as structurally non-equilibrium. Their fusion leads to a catastrophic enhancement of up-conversion, and at high erbium concentrations to phase segregation, accompanied by a dramatic decrease in quantum excitation efficiency of the main laser transition in Er^{3+} [3].

Among erbium-doped structurally non-equilibrium silicates investigated earlier [2,3], Er^{3+} luminescence spectra in SiO_2 with fluorine additive display an interesting feature. Instead of the non-homogeneously broadened and thus poorly resolved structure of Starks manifolds typical for glass hosts [6,7], erbium photoluminescence spectra in this host consist in a set of relatively narrow bands. This means that in the vicinity of each erbium ion a stable, ordered atomic neighboring is formed, which is weakly affected by electric field fluctuations caused by the disorder in amorphous host as a whole.

The current research attempts to find the origin of the ordered structure responsible for anomallously narrow Er^{3+} ion Stark emission lines observed in non-fused amorphous silicon dioxide with fluorine additive. For this purpose we synthesize by the plasma chemical method a set of erbium-doped fluorine containing silica samples at an average substrate temperature of about 1150 °C. Photoluminescence spectra and kinetics of the samples obtained are studied using excitation from both an Ar^+ ion laser at a wavelength of 514.5 nm and a diode laser at a wavelength of 975 nm. Measurements are performed at temperatures ranging from 27 to 300 K. Using X-ray diffraction structural analysis, an attempt to discover and to identify a crystalline phase in the synthesized samples is performed. The fusion and annealing effects of the amorphous composites on Er^{3+} luminescent properties are studied.

2. Experimental set-ups, methods and samples

Detailed description of the equipment and the principle of glass deposition one can find in [2,3]. Here we restrict our consideration only to a sketchy outline of key points of the technology. Synthesis of doped glass is conducted via oxidation of $SiCl_4$ and $ErCl_3$ vapors mixture by the microwave-induced discharge in oxygen ambient with addition of CF_4. Total pressure of the mixture is 1 torr. Mixed reagents are continuously fed through a silica substrate tube towards a plasma column, the length of the latter being periodically changed (the SPCVD process [8]). Erbium and fluorine doped silicon dioxide in the form of transparent amorphous material is deposited layer-by-layer on the inner surface of a part of the substrate tube in the region of plasma column scanning. The part of the tube with deposition zone 30 cm in length is placed in a furnace. The temperature of the outer surface of the tube in the middle of the deposition zone is measured by an optical pyrometer installed in a feedback loop of a temperature controller. The entire material deposition process required 1.5 h.

Samples for the investigation are transverse slices of the substrate tube with a 150–200 μm thick layer of amorphous material deposited on the inner surface. Typical of SPCVD variation in scanning plasma exposure duration of different parts of the inner surface of the substrate tube causes some difference in an effective deposition temperature in these parts. Keeping in mind a strong dependence of the glass structure on a deposition temperature, samples for further spectroscopic study are cut from several cross-sections separated from each other by a distance of ~10 cm. Glass composition in each section is determined by an X-ray micro-analyzer of JEOL JSM-5910LV electron microscope (see Table 1). We estimate that for samples cut from different cross-sections the difference in deposition temperature reaches ~50 °C.

Photoluminescence signals are detected with the help of the experimental set up described earlier [2,3]. The set up has been additionally equipped with a 'cold finger' optical cryostat to provide measurements at low temperatures. Temperature of the cold finger is controlled by a Cu–Cu:Fe thermocouple with a measuring junction connected near the sample holder. A reference junction of the thermocouple is thermostated in a Dewar vessel with melting ice. Inaccuracy in the temperature measurement does not exceed 2 °C. Luminescence kinetics is recorded by a PC-compatible 12 bit analog to digital converter (ADC), which allows synchronous acquisition and averaging of dataflow cycles from a pulsed-periodic process by a PC. The ADC yields temporal resolution >2 μs, the time constant of an analog signal preamplifier being 50 μs. Average powers of modulated laser pumps are 250 mW for Ar^+ and 150 mW for diode lasers. The diameter of pump beams at the entrance to the sample is ~150 μm.

To tailor the effect of subsequent fusion on Er^{3+} luminescence in fluorine-doped silica obtained by the plasma chemical deposition, a local laser heating of samples is

Table 1
Deposition conditions and compositions of samples

Sample	T_{depos} (°C)	F (wt%)	Er, at. ppm
#1	$1150 - \Delta$	3.5	800
#2	1150	3.2	650
#3	$1150 + \Delta$	2	800