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Fabrication and characterization of Er^{+3} doped SiO_2/SnO_2 glass-ceramic thin films for planar waveguide applications

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Abstract: Glass-ceramics are a kind of two-phase materials constituted by nanocrystals embedded in a glass matrix and the respective volume fractions of crystalline and amorphous phase determine the properties of the glass-ceramics. Among these properties transparency is crucial in particular when confined structures, such as, dielectric optical waveguides, are considered. Moreover, the segregation of dopant rare-earth ions, like erbium, in low phonon energy crystalline medium makes these structures more promising in the development of waveguide amplifiers. Here we are proposing a new class of low phonon energy tin oxide semiconductor medium doped silicate based planar waveguides. Er^{3+} doped (100-x) SiO_2-$x$$SnO_2$ (x= 10, 20, 25 and 30mol%), glass-ceramic planar waveguide thin films were fabricated by a simple sol-gel processing and dip coating technique. XRD and HRTEM studies indicates the glass-ceramic phase of the film and the dispersion of ~4nm diameter of tin oxide nanocrystals in the amorphous phase of silica. The spectroscopic assessment indicates the distribution of the dopant erbium ions in the crystalline medium of tin oxide. The observed low losses, 0.5±0.2 dB/cm, at 1.54 μm communication wavelength makes them a quite promising material for the development of high gain integrated optical amplifiers.

1. Introduction

Glass-ceramics (GC) are nanocomposite materials and have been an intensive topic of research with their specific characteristics of capital importance in photonics. These systems, depending on their glass host and crystalline phase compositions, show improved mechanical, thermal, electrical and optical properties. The applications of GCs have spread over several areas like cook-top panels, electronics, medicine and dentistry, tough GCs and optical materials. The silica based glass ceramic (GC) systems has attracted great attention with the idea of Tick et al., [1] on the possibility of using such GCs as low-loss optical waveguides. The interesting optical property of these systems is the crystal like spectroscopic properties for the segregated optically active dopant ions in the low phonon energy crystalline phase. Especially, reduction in the inhomogeneous line width and therefore to an increase in the emission and absorption cross-sections of the active ions [2-3]. This behavior would thus make these materials attractive host for the rare-earth ions, which play an important role at the

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telecommunication wavelength of 1.54μm. In this regard erbium doped fiber amplifiers (EDFA) and erbium doped waveguide amplifiers (EDWA) are well-known for the past few decades, with the erbium ions' intra 4*f* emission at 1.54μm. From the past few decades several GC phase systems with low phonon energies of crystalline phase were developed like silica-titania, silica-oxyfluoride, silica-hafnia etc., by our group,[4-8] with the objective of meeting the low optical losses and higher band width and gain. Here we would like to propose a GC phase of erbium doped silica-tin oxide matrix with the low optical losses for 1.54 μm wavelength propagation towards applications in the EDWAs.

2. Fabrication of planar waveguide structures

Once the ethanolic colloidal suspension prepared by using precursor $SnCl_2 \cdot 2H_2O$ becomes transparent, erbium ions were introduced through $Er(NO_3)_3.5H_2O$. The molar concentration of Er^{3+} in the total composition was maintained as 0.3 or 1 mol%. The silica solution obtained by mixing tetraethylorthosilicate (TEOS), ethanol (EtOH), deionized water and hydrochloric acid (HCl) as a catalyst was prehydrolyzed for 1h at 65 °C. A ratio of 1:0.01:2, was used for the TEOS: HCl: H_2O mixture. The quantity of ethanol during the preparation of the two solutions was chosen such that we maintain a concentration of (SnO_2+SiO_2) in ethanol as 0.448 mol/L. The two solutions were mixed and left at room temperature under stirring for 16 h. The resulting sol was filtered and then deposited on pure vitreous SiO_2 (v-SiO_2) by dip-coating, with a dipping rate of 40 mm/min. Each layer was annealed at 900 °C for 3 min prior to the application of the next coat. After every five the resulted film was heat treated again at 900 °C for 5min. Finally the films with Si/Sn molar ratios 90/10, 80/20 and 75/25 were heat treated at 900 °C for 30h, 20h and 5min respectively for attaining the densified and crack-free uniform thin films.

3. Results and Discussion

X-ray diffraction (XRD) spectra showed in figure 1a was measured with grazing angle of incidence of the beam at 1°. The spectra is composed of the diffraction peaks corresponding to single crystals of SnO_2 in tetragonal (cassiterite) phase [9] and a broad band centered at 21.5° corresponding to amorphous silica phase. The peak corresponding to (211) plane of the XRD spectrum (figure 1a) was used to determine the nanocrystals size by using the well-known Debye-Sherrer formula [9]. The size of nanocrystals was found to be ~4nm for the 25% SnO_2 content waveguide. Figure 1b shows the high resolution transmission electron microscope (HRTEM) image for x= 25 mol% SnO_2 content waveguide. Figure 1b also shows the narrow size distribution and lattice fringes of SnO_2 ~4 nm nanocrystals. The selected area electron diffraction (SAED) pattern shown in the inset of figure 1b indicates the polycrystalline nature of SnO_2.

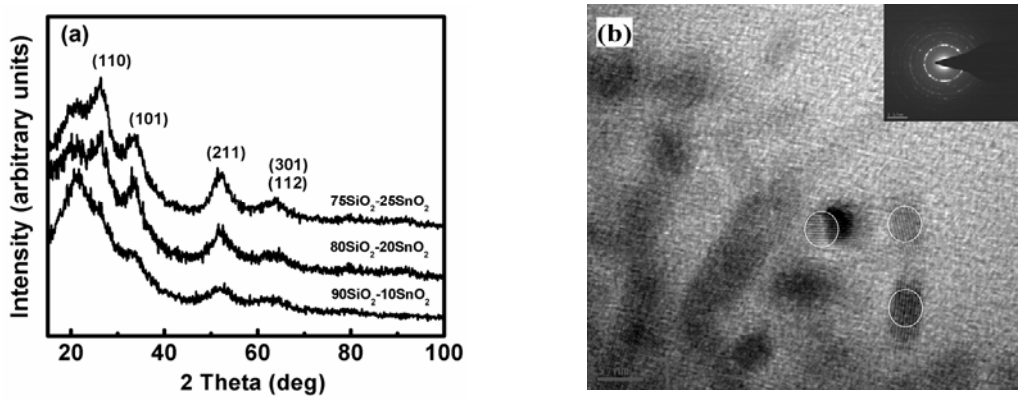

Figure 1.(a) GIXRD spectra measured with grazing angle of incidence at 1°. (b) HRTEM image and corresponding SAED pattern (in the inset) shows the tin oxide nanocrystals distribution in a thin film.

The energy band gap of embedded semiconductor SnO_2 nanocrystals could be obtained by plotting the well-known Tauc relation [10]. SnO_2 is known for its direct band gap and dipole forbidden transition in the UV region [10-11]. The plot of $(\alpha h\nu)^{2/3}$ vs $h\nu$ is shown in the figure 2a. The estimated energy band gap for all the three compositions, which is around 3.75eV, indicates the quantum confinement effect [12] and unique size distribution in all three compositions with a variation in the density of the particles.

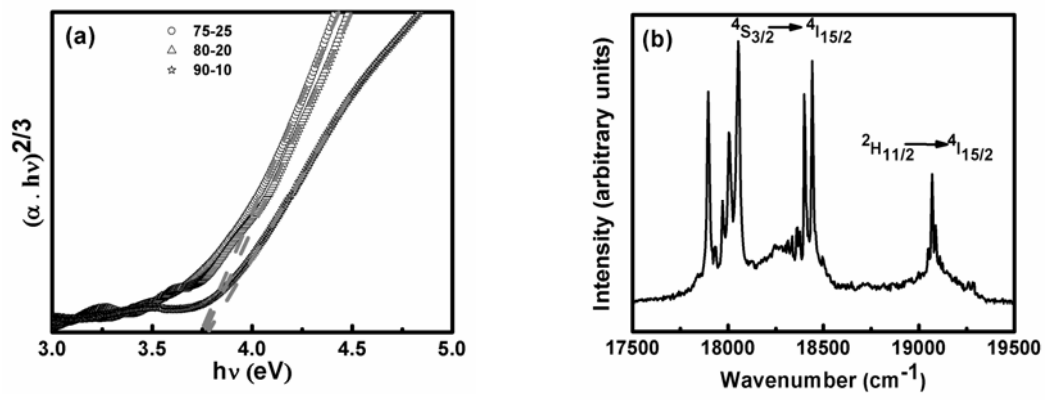

Figure 2: a) Plot of $(\alpha h\nu)^{2/3}$ vs $h\nu$ of Tauc plot for three compositions of SiO_2:SnO_2. The extrapolation of dashed line to $(\alpha h\nu)^{2/3} = 0$ axis gives the value of the band gap of the sample. (b) Photoluminescence spectra in the visible range of the 0.3mol% Er^{3+}-activated $75SiO_2$-$25SnO_2$ planar waveguide. Excitation was performed at 488nm, in the TE_0 mode configuration.

Figure 2b shows the photoluminescence (PL) in the visible range of erbium ions on excitation with the 488nm of Argon ion laser. The presence of narrow structures and the important reduction in the usual inhomogeneous line width of the erbium ions emission in the luminescence spectra (figure 2b) indicates a crystalline local environment for the Er^{3+} ion [12]. The crystal-field strength experienced by the optically active ions directly reflects the maximum energy splitting of the stark components of the electronic level. In fact, the narrowing is more evident in the visible PL spectra for the $^4S_{3/2}\rightarrow{}^4I_{15/2}$, and $^2H_{11/2}\rightarrow{}^4I_{15/2}$ transitions. The later transition is hypersensitive and therefore particularly suitable to detect the change in the environment immediately around the Er^{3+} ion [3]. So the presence of nanocrystals is a factor responsible for the reduction in the inhomogeneous line width, as observed in the present case figure 2b.

Table 1: Optical parameters of the 1mol% Er^{3+} activated $75SiO_2$-$25SnO_2$ planar waveguides. The thickness of the film found to be 1.15(±0.05) microns.

Wavelength (nm)	632.8	1319	1542
Refractive index (TE) (±0.001)	1.566	1.551	1.547
No. of modes	2	1	1
Attenuation coefficient (±0.3dB/cm)	0.7	0.6	0.5

The thickness and refractive index of the thin films were measured by m-line technique based on prism coupling method [8]. An increase in the refractive index value was observed as a function of

increase in SnO_2 content. The maximum percentage of SnO_2 in silica matrix to support the propagation modes was found to be x=25%. The thickness and refractive index values for x=25% of SnO_2 are reported in table 1 for three different wavelengths of propagation. The attenuation coefficient (losses for the guided mode) was determined by collecting the scattered light along the propagating TE_0 mode. The observed refractive index values for TE and TM modes are in good agreement with the Lorentz-Lorentz equation with n= 1.457 and n= 1.94 for silica and tin oxide respectively. From the TE and TM measurement of refractive index values it is evident that birefringence is absent in the system [13]. The maximum confinement of the TE_0 mode at 1542nm was found to be about 82%. The attenuation coefficient measurements were performed by scanning the intensity of the signal along the propagating mode with the help of a fiber probe coupled to a detector. Observed low optical losses of 0.5±0.2dB/cm at 1.54μm wavelength propagation makes this 75/25 silica-tin oxide nano structure waveguides as the most promising system for integrated optical amplifiers.

4. Conclusions

In summary, we have fabricated erbium doped SiO_2-SnO_2 glass-ceramic waveguides with a maximum molar composition of SnO_2 at 25 mol%. From the structural and optical assessment the size of SnO_2 nanocrystals was found to be ~4 nm in diameter and energy band gap of 3.75eV. The spectroscopic assessment in the visible and NIR range indicates the local SnO_2 crystalline environment for the erbium ions. From the optical and spectroscopic results, RE-activated SnO_2 glass-ceramic waveguides with low attenuation coefficient of 0.5±0.2dB/cm at 1.54μm appears to be a viable system for integrated optics.

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