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Photoluminescence in pulsed-laser deposited GeGaSbS:Er films

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ABSTRACT

The complex dielectric function, the Er^{3+} Stokes emission at ≈1540 nm and the upconversion photoluminescence at ≈990 nm of pulsed-laser deposited thin-film GeGaSbS:Er^{3+} are studied. The linear-refractive-index dispersion is obtained by fitting spectroscopic ellipsometry data to the Sellmeier and the Cody-Lorentz parametrizations. The former model is used to calculate nonlinear refractive index. The Stokes emission intensity at ≈1540 nm, originating from the Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition under a 980 nm pumping, diminishes with increasing refractive index and decreasing optical-bandgap energy of the films. An attempt to relate differences in the optical and photoluminescence properties to the atomic structure elucidated from Raman spectra analysis is presented. The emission probability is highest for the structure with the lowest fraction of (semi)metallic bonds, the highest content of homonuclear S-S bonds and the lowest Ge/S ratio. In such a film, the clustering of Er^{3+} ions, which is responsible for the intensity weakening, is suppressed. The film shows ≈990 nm upconversion photoluminescence originating from the Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition under a 1550 nm excitation. The upconversion peak shape resembles that of the compositionally and structurally similar bulk glass.

1. Introduction

Rare-earth-(RE)-ion-doped sulfide-based chalcogenide glasses (ChGs), for which the archetype is Ga-Ge-(As,Sb)-S system, are promising materials for a number of photonic applications such as fibers, planar waveguides, detectors, lasers and so on [1]. Apart from the resistance to crystallization, the sulfide-based ChGs are attractive because of the well-balanced combination among various optical properties. In particular, they exhibit a wide-transparency window ranging from the visible to the mid-infrared (IR) spectral region, which results from the low phonon energy of $< \sim 400\,cm^{-1}$, and they are characterized by high refractive indices ($n > 2$) in the near-IR region [2], which in conjunction with the transparency are essential properties for specific photonic applications. Erbium is probably the most thoroughly studied dopant, whose structural role has largely been appreciated. The low phonon energy suppresses any nonradiative recombination probability and as a consequence, for example, the efficiency of the nonradiative Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition involved is reduced and the ≈1540 nm emission decay depends on the pumping source energy [3]. The high n promotes radiative recombination probability in RE^{3+} ions [2].

In addition to the above, ChGs are photosensitive when exposed to light with energy corresponding to the near- and above-bandgap energy of the glass [2]. The photoexcited glasses may exhibit wide-continuum [4] and third-harmonic generations [5] because of high values of the nonlinear refractive index, n_2 [6]. Chalcogenide glasses are also optically active when defect states, represented by the Urbach energy, are excited [7]. Rare-earth-doped glasses exhibiting photoluminescence (PL) emission at ≈1540 nm have been intensively studied for potential amplification applications in the telecommunication *C*-band 'Erbium window', $\lambda = 1530–1565$ nm [8,9].

Chalcogenide glasses containing Ga can host up to ~2 at. % of RE ions in GeGaS [10,11] and GeGaSe bulk glasses [12] avoiding crystallization on moderate cooling of the melt [8]. Gallium atoms, typically present as $GaS(Se)_{4/2}$-tetrahedral-structural sites, play an important structural role for accommodating RE ions in the glassy matrix; it is understood that Er^{3+} ions are spatially correlated with Ga sites [11,12]. For nonstoichiometric GaGeSe glasses with Ga content of 9 at. % and higher, Munzar et al. [12] suggested that the increasing content of the

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homonuclear bonds Ge-Ge, for example in ethane-like units are formed at the expense of corner-sharing tetrahedra, and Ga-Ga bonding (indistinguishable from Ge-Ge by Raman spectroscopy) probably leads to nonuniform distribution of Er^{3+} in the matrix and to concentration quenching of PL [8]. Such a site preference of optically-active ions is also known for oxide glasses. Recent work by Gao et al. [13] shows that PL-active ions, transition metals (Ni^{2+} and Cr^{3+}) and rare earths (Yb^{3+} and Er^{3+}), can be selectively doped in different nanocrystalline phases in silica-based glass-ceramics. Addition of Sb not only improves thermal stability and resistance to moisture [14,15], but also results in a high nonlinear susceptibility and Raman gain coefficients [6] of GeGaS glasses.

Compared to bulk glasses, upconversion photoluminescence (UCPL), unlike PL [3], is more difficult to detect in thin-film amorphous (a-) a-chalcogenides because of a low absorption cross-section and generally lower probability of anti-Stokes processes. Pollard et al. [16] observed UCPL for sputtered a-GaLaSO:Er^{3+} films, 150 nm thick, annealed at elevated temperatures up to 600 °C. However, at such elevated temperature the films may contain nanocrystalline particles enhancing the emission. Nazabal et al. [17] demonstrated the green Er^{3+} UCPL, pumped at $\lambda_{exc} = 804$ nm, for sputtered $Ga_5Ge_{20}Sb_{10}S_{65}$:Er^{3+} (here and throughout in at.%) rib waveguide, an etched thickness of 2 μm and 10 μm in width.

The focus of this work is on exploring how the amorphous structure of pulsed-laser deposited (PLD) GeGaSbS:Er^{3+} films influences the optical properties, the Er^{3+} ≈1540 nm Stokes PL and the ≈990 nm near-IR UCPL emissions. As the bulk glasses were studied in Ref. [18], the interest here is in their corresponding films which may potentially be integrated on chips for all-optical networks [19]. The optical functions of the as-deposited films are obtained by fitting spectroscopic ellipsometry (SE) data to the Cody-Lorentz [20] and the Sellmeier [21] models. Difference of $\Delta n \approx 0.3$ ($\lambda = 1550$ nm) and $\Delta n_2 \approx 7.5 \times 10^{-11}$ esu can be achieved by altering the Ga/Sb, Ge/S and (Ga + Ge + Sb)/S atomic ratios; the compositional changes are by no more than 10 at. % of the individual elements in a host matrix. All the studied as-deposited films show the Stokes PL emission at ≈1540 nm for $\lambda_{exc} = 980$ nm. The as-deposited film $Ge_{25}Ga_6Sb_6S_{63}$:Er, the composition with the lowest n, the highest optical-bandgap energy E_g, the lowest content of (semi)metallic and detectable presence of homonuclear S-S bonds, is the only one showing appreciable UCPL at ≈990 nm by using $\lambda_{exc} = 1550$ nm excitation.

2. Experimental details

Five host bulk matrices corresponding to three nominal compositional series are studied: (1) $Ge_{25}Ga_{10-x}Sb_xS_{65}$ with $x = 0.5$, 2.5 and 5.0 at. %; (2) $Ge_{25-x}Ga_{7.5}Sb_{2.5}S_{65+x}$ with $x = 5.0$ at. %; and (3) $(Ge_{25}Ga_5Sb_5S_{65})_{1-x}S_x$ with $x = 0.285$, i.e. $Ge_{17.8}Ga_{3.6}Sb_{3.6}S_{75}$; these glasses are doped with 0.5 at. % of Er. The bulk glasses were synthesized by a standard melt-quenching technique from high-purity elements, see Ref. [18] for details.

The glasses were used as the targets for PLD. The deposition was done using a KrF excimer laser (Lambda Physik COMPex) operating at $\lambda \approx 248$ nm with a pulse energy of 220 mJ, a pulse length of 30 ns, a repetition rate of 20 s^{-1} and a laser spot area of ≈2.4 mm^2. A deposition base pressure of 10^{-3} Pa was used and films were deposited on cleaned microscope slides.

The composition was checked by using an energy-dispersive-X-ray microanalyzer IXRF system with a detector GRESHAM Sirius 10, which is a part of SEM JSM-5500LV JEOL.

Film thickness, d_f, and optical properties of the as-deposited PLD films were measured by a variable-angle-spectroscopic ellipsometry (VASE®), J.A.Woollam, Co., Inc. in the spectral range of 300–2300 nm (4.13–0.54 eV) at the angles of incidence AOI = 70 and 75 deg (Sect. 3.1). Surface roughness, d_r, was calculated by using an effective-medium approximation [22].

Table 1
The composition of the as-deposited thin-film GeGaSbS:Er^{3+} (± 1 at. %). The Er^{3+} content could not be obtained accurately.

Nominal/target composition	PLD thin films (at. %)			
	Ge	Ga	Sb	S
$Ge_{25}Ga_5Sb_5S_{65}$:$Er_{0.5}$	30	7	7	56
$Ge_{25}Ga_{7.5}Sb_{2.5}S_{65}$:$Er_{0.5}$	30	11	4	55
$Ge_{25}Ga_{9.5}Sb_{0.5}S_{65}$:$Er_{0.5}$	29	13	1	57
$Ge_{20}Ga_{7.5}Sb_{2.5}S_{70}$:$Er_{0.5}$	24	12	4	60
$Ge_{17.8}Ga_{3.6}Sb_{3.6}S_{75}$:$Er_{0.5}$	25	6	6	63

The structure of the targets and of the as-deposited PLD films was investigated by Raman scattering using a UV-LabRam (Jobin-Yvon HR800) micro-Raman spectrometer equipped with a HeCd laser ($\lambda = 441.6$ nm) with a low-power density ($\sim 10^3$ W cm^{-2}) to avoid photoinduced effects [23] (Sect. 3.3).

Near-IR Stokes PL emission and UCPL spectra (Sect. 3.4) were measured with 75 mW diode lasers operating at $\lambda_{exc} = 980$ and 1550 nm, 1/2 m monochromator, photomultiplier tube and a cooled Ge detector [18].

3. Results and discussion

The amorphicity of the as-deposited films was confirmed by X-ray diffraction (not shown here). The compositional analysis shows that the PLD films are deficient in sulfur by ~10 at. % in comparison to their corresponding targets, see Table 1. This is a typical issue in PLD-prepared films and sulfur-deficient films were also observed for the binary A_2S_3 [24], ternary AgAsS [25,26] and GaLaS [27], and quaternary GeGaSbS [28,29] targets. The studied bulk glasses are referred to their nominal compositions as GeGaSbS:$\mathbf{Er_{0.5}}$; the thin-film compositions refer to those in Table 2, expressed as GeGaSbS:**Er**, and the content of Er^{3+} ions is assumed to be close to the nominal value of 0.5 at. %.

3.1. Spectroscopic ellipsometry

The measured SE parameters, tanΨ (the ratio of the amplitudes of the perpendicularly polarized waves after their reflection off the sample surface) and Δ (the amplitude shift between the reflected waves), were fitted to the Sellmeier model [21] in the transparent region between 1000 and 2300 nm and to the Cody-Lorentz (CL) model [20] in the entire spectral range. The latter model, developed by Ferlauto et al. [20], can describe the optical functions of a-chalcogenides from transparent to interband absorption regions taking into the account the presence of Urbach tail (Eq. (1a)). The model was shown to be very accurate in describing the dielectric functions, for example, of thin-film a-$Ge_2Sb_2Te_5$ [30]. The imaginary part ε_2 of the complex dielectric function ε is according to Ferlauto et al. [20] given as:

$$\varepsilon_2(E) = \frac{E_1}{E}\exp\left(\frac{E - E_t}{E_u}\right) \text{ between } 0 < E \le E_t, \tag{1a}$$

$$\varepsilon_2(E) = G(E) \times L(E) = \frac{(E - E_g)^2}{(E - E_g)^2 + E_p^2} \times \frac{A_{CL}E_n\Gamma E}{(E^2 - E_n^2)^2 + \Gamma^2E^2} \text{ for } E > E_t, \tag{1b}$$

where A_{CL} is the amplitude, E_n is the peak-transition energy and Γ is the broadening of the Lorentz-oscillator function, E_g is the optical-bandgap energy, E_t is the transition between the Urbach tail and the band-to-band absorptions, E_u is the Urbach energy (the width of the weak absorption) and E_p is the transition energy separating the absorption-onset behavior $G(E)$ for $E < E_p + E_g$ from the Lorentz-oscillator behavior $L(E)$ for $E > E_p + E_g$. The imaginary part ε_2 is a continuous function at $E = E_t$, and the energy E_1 is defined as: