Thin Solid Films 518 (2010) 4941–4947

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Optical waveguide based on amorphous $Er^{3+}$-doped Ga–Ge–Sb–S(Se) pulsed laser deposited thin films

V. Nazabal [a,*], P. Němec [b], A.M Jurdyc [c], S. Zhang [a], F. Charpentier [a], H. Lhermite [d], J. Charrier [e], J.P. Guin [f], A. Moreac [g], M. Frumar [b], J.-L. Adam [a]

[a] Sciences Chimiques de Rennes (SCR), UMR CNRS 6226, Equipe Verres et Céramiques, Université de Rennes 1, Rennes, France
[b] Department of General and Inorganic Chemistry and Research Center, Faculty of Chemical Technology, University of Pardubice, Legions Sq. 565, 53210, Pardubice, Czech Republic
[c] Laboratoire de Physico-Chimie des Matériaux Luminescents (LPCML), UMR CNRS 5620, Université Claude Bernard-Lyon 1, Villeurbanne, France
[d] IETR-Microelectronique, UMR CNRS 6251, Université de Rennes 1, 35042 Rennes, France
[e] FOTON, UMR 6082-ENSSAT, UMR CNRS 6251, Université de Rennes 1, 35042 Rennes, France
[f] LARMAUR, UMR CNRS 6251, Université de Rennes 1, 35042 Rennes, France
[g] Institut de Physique de Rennes, UMR CNRS 6251, Université de Rennes 1, 35042 Rennes, France

ARTICLE INFO

*Article history:*
Received 9 November 2008
Received in revised form 3 March 2010
Accepted 11 March 2010
Available online 19 March 2010

*Keywords:*
Amorphous materials
Chalcogenide sulphide
Thin films
Pulsed laser deposition
Optical properties
Rare earth compounds
photoluminescence

ABSTRACT

Amorphous chalcogenide films play a motivating role in the development of integrated planar optical circuits due to their potential functionality in near infrared (IR) and mid-IR spectral regions. More specifically, the photoluminescence of rare earth ions in amorphous chalcogenide films can be used in laser and amplifier devices in the IR spectral domain. The aim of the present investigation was to optimize the deposition conditions for the fabrication of undoped and $Er^{3+}$ doped sulphide and selenide thin films with nominal composition $Ga_5Ge_{20}Sb_{10}S(Se)_{65}$ or $Ga_5Ge_{23}Sb_5S_{67}$ by pulsed laser deposition (PLD). The study of compositional, morphological and structural characteristics of the layers was realized by scanning electron microscopy–energy dispersive spectroscopy, atomic force microscopy and Raman spectroscopy analyses, respectively. Some optical properties (transmittance, index of refraction, optical band gap, etc.) of prepared chalcogenide films and optical losses were investigated as well. The clear identification of near-IR photoluminescence of $Er^{3+}$ ions was obtained for both selenide and sulphide films. The decay of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition at 1.54 μm in $Er^{3+}$ doped $Ga_5Ge_{20}Sb_{10}S_{65}$ PLD sulphide films was studied to assess the effects of film thickness, rare earth concentration and multilayer PLD deposition on their spectroscopic properties.



## 1. Introduction

Because of their potential functionality in the near and mid-IR, chalcogenide glasses are attractive materials in the area of optics, optical imaging and data storage. They show remarkable properties like large IR spectral range of transparency (up to 10–20 μm), low phonon energy, photosensitivity and high linear and non-linear refractive index. In the form of amorphous thin films, chalcogenides are attractive for the development of integrated optics or optical coatings [1–7].

In the field of active optics, the low phonon energy of chalcogenide hosts warrants a low probability of multiphonon relaxations between the energy levels of trivalent rare earth ions ($RE^{3+}$). Thus, the radiative efficiencies of the most rare earth emissions in near and mid-IR, for which the upper levels can be easily non-radiatively quenched by multiphonon transitions, are improved [8–10].

A key stage in this research area is the preparation of thin films with required chemical composition and appropriate physical properties. For the preparation of amorphous layers with multi-component composition, pulsed laser deposition (PLD) is one of the most efficient and flexible methods [11]. To date, the photoluminescence of erbium in sulphide or selenide films has been characterized essentially for sputtered or evaporated films [5,12–15], and very rarely for PLD films [16]. The measurement of decay lifetime in $Er^{3+}$ doped PLD films has never been reported in the literature.

The aim of the present investigation is to optimize the deposition conditions of undoped and $Er^{3+}$ doped sulphide and selenide films of the Ga–Ge–Sb–S(Se) system and to analyze their physical properties such as chemical composition, structure and optical properties. Especially, the photoluminescence (PL) properties of the $Er^{3+}$ doped films and the decay times were investigated. For a first evaluation of PL in $Er^{3+}$ doped $Ga_5Ge_{20}Sb_{10}S(Se)_{65}$, the choice of sulphide films was motivated by limiting the possible interactions between the glass host matrix and erbium ions when broad-band excitation is used. In previous studies of $Er^{3+}$ doped $As_{12}Ge_{33}S(Se)_{55}$ glasses, a broad excitation band due to the absorption of light by the host glass was observed in the photoluminescence excitation (PLE) spectra at low

* Corresponding author.
*E-mail address:* virginie.nazabal@univ-rennes1.fr (V. Nazabal).

0040-6090/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2010.03.030

temperature [17,18]. The PLE spectrum of the 1550 nm $Er^{3+}$ emission contains a superposition of relatively sharp peaks related to the characteristic $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^4I_{15/2} \rightarrow {}^4I_{9/2}$ absorption bands of trivalent erbium at 810 and 980 nm, respectively, and a broad, below-gap PLE band in the range of 400–700 nm for sulphide and 600–1000 nm for selenide glasses. Consequently, in this paper, we focused on sulphide films permitting excitation at 980 or 800 nm, without any influence of light absorption by the host matrix.

## 2. Experimental details

The glasses with nominal compositions of $Ga_5Ge_{20}Sb_{10}S(Se)_{65}$ and $Ga_5Ge_{23}Sb_5S_{67}$, undoped and doped with $Er^{3+}$ (0.3, 0.7, 1.4 wt.% for sulphide and 1.0 wt.% for selenide glasses), were prepared by means of conventional melt and quenching method. High purity elements (5–6 N) were weighted in a dry glove box, introduced in a fused silica ampoule and pumped under vacuum of $10^{-3}$ Pa for a few hours. Then, the sealed tubes were heated in a rocking furnace, to ensure the homogenization of the melt, at 900 °C for 12 h. After the quenching, the glass rods were annealed below the glass transition temperature ($T_g \sim 305$ °C and $T_g \sim 280$ C for sulphide and selenide glasses, respectively) for 3 h.

The targets for PLD were prepared in the form of the glass cylinders, 2–4 mm thick with a 25 mm diameter. The deposition of thin films was carried out on chemically cleaned microscope glass slides, silicon or $SiO_2$/Si substrates at room temperature.

After an optimization procedure, the targets were ablated using a KrF excimer laser, operating at the wavelength of 248 nm, with constant output energy of 200 mJ per pulse and 30 ns pulse duration. The laser energy fluency was set at 1 or 0.5 J $cm^{-2}$. Laser pulses were directed on the target at the repetition rate of 20 Hz with a pressure in the vacuum chamber about $5.5–6 \times 10^{-4}$ Pa. The off-axis PLD technique combining rotating substrates and scanning of the targets ($\sim 1 \times 1.2$ $cm^2$ area) by the laser beam was employed for the fabrication of appropriate quality films in terms of the homogeneity in thickness.

The chemical composition of the films and the targets was studied using scanning electron microscopy with an energy-dispersive X-ray analyzer (SEM–EDS, JEOL JSM 6400-OXFORD Link INCA). The morphology and the structure of the amorphous films were analyzed by atomic force microscopy (AFM, Nanoscope III, Digital Instruments, Budgdet Sensors Tap300Al with radius <10 nm), in mode tapping with resonance frequency of 300 kHz, scanning electron microscopy (SEM, JEOL JSM 6301F) and micro-Raman analysis were performed using a triple Raman-spectrometer (XY-DILOR, substractive mode, resolution around 1.5 $cm^{-1}$ per pixel) coupled to a Titanium–sapphire laser (excitation line at 720 nm). To avoid sample heating, optical density filters have been used to reduce laser power focused on the sample. In order to minimize the effect of the thermal population at low wavenumbers, the reduced Raman intensities were calculated, defined as $I_{red}(\omega) = I(\omega) \cdot \omega / [n(\omega) + 1]$ [19]. The $I(\omega)$ term represents experimental Raman intensity at $\omega$ frequency and $n(\omega)$ is the Bose–Einstein factor, given by $n(\omega) = (\exp[(\hbar\omega / k_B T) - 1])^{-1}$. The reduced Raman spectra are decomposed into a set of Gaussian peaks and the results of fitting are presented. The average film thickness was controlled by a variable-angle spectroscopic ellipsometer (VASE).

A classical photolithography process with dry etching employing a positive (S1813) photoresist was used to prepare rib waveguide. The process consists, first, in the exposure of the photoresist through a Cr-mask thanks to an i-line mask aligner. After post-exposure-bake, the exposed bands were dissolved with a suitable developer that takes advantage of the high reactivity of chalcogenide films with most of the alkaline solutions. After hard-bake, the films were etched by the reactive ion etching (RIE) using a $CF_4$ plasma to achieve vertical and smooth side. The gas flux varied from 3 to 30 sccm, gas pressure was changed between 3 and 30 mTorr and RF power range of about 30–300 W was used. The fluorine-based gases were selected since $F^-$ ions can form volatile species. The etch rates were determined by observation of the film cross-sections with SEM.

The refractive indices of sulphide and selenide films were measured by means of VASE. The measurements were performed by a J. A. Woollam Co., Inc. ellipsometer with an automatic rotating analyzer in the spectral range of 500–2300 nm typically, at angles of incidence 65–75°. The spectra were usually measured with 10 nm steps. The ellipsometer is equipped with AutoRetarder®, which allows the measurement of the ellipsometric parameter Δ at a 360° interval. The ellipsometric data in the weak absorbing region were analyzed by a model consisting in the description of the substrate, the film (employing Cauchy dispersion formula, i.e. $n = A + B/\lambda^2 + C/\lambda^4$, where $n$ is refractive index, $A$, $B$ and $C$ are constants, λ is the wavelength) and the surface roughness layer (defined by using effective medium approximation). The transmission spectra of the thin films from the Ga–Ge–Sb–S(Se) system were recorded by a spectrophotometer in the 400–2000 nm spectral range. Optical losses were evaluated by studying the scattered light from the surface of the waveguide varied in length from 2 cm [20,21]. The laser light was coupled into the waveguide by means of a single-mode fiber. The intensity of the scattered light was recorded with a digital camera placed above the sample. Transverse scanning along the light propagation direction enabled us to obtain the 2-D light intensity distribution of the waveguide modes. The longitudinal variation was obtained by integrating the data along each sampling transverse line. The light intensity decreased exponentially with the $z$-propagation distance. In this study, the attenuation values were the average of several measurements. The polarization of the coupled light into the waveguide was not controlled. In addition, light propagation was observed at the output of the waveguides by the near field profiles of guided modes at 1550 nm.

For the photoluminescence experiments, in a first approach, a continuous wave $Nd^{3+}$:YAG laser (1064 nm) with a pump power of 100 mW was used for the excitation of $Er^{3+}$ ions in thin films. For the detection of luminescence, a liquid-nitrogen-cooled Ge detector was used. For a detailed fluorescence characterization, a Ti:sapphire laser ($\lambda_{exc} = 795$ nm; $P_{exc} = 250$ mW), pumped by an $Ar^+$ laser, was used for the excitation of $Er^{3+}$ doped thin films and targets. Finally, an argon laser (488 nm, 10 mW) with a diameter of ~1.5 mm was also used. The beam was not focused on the sample and the incidence angle of the laser was almost grazing to reduce the reabsorption. A Jobin-Yvon monochromator (H25-1, 600 g/mm, blazed at 1000 nm) and a germanium photodiode with a synchronic detection were used to analyze the fluorescence in the 950–1750 nm spectral region. The excitation laser wavelength was removed in front of the monochromator by a silicon filter. The spectral resolution of PL set-up was better than 10 nm. The spectra were corrected in wavelength by the calibration with erbium emission spectra of $LiYF_4$ between 1400 and 1600 nm. The lifetime measurements of $Er^{3+}$ PLD sulphide films were performed with an excitation at 980 nm from a $Nd^{3+}$:YAG-pumped OPO laser (few ns pulses), with an InGaAs detector interfaced to a numerical oscilloscope.

## 3. Results and discussion

A detailed study of the morphological, compositional and structural characteristics of prepared thin films as a function of the deposition conditions was carried out, with the final objective to realize a planar and ridge optical waveguides presenting fluorescence in the near-IR spectral range.

### 3.1. Chemical composition of the films and bulk glassy targets

The $Ga_5Ge_{20}Sb_{10}S(Se)_{65}$ and $Ga_5Ge_{23}Sb_5S_{67}$ glass compositions were chosen as the starting materials because of their interesting