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Luminescence of rare earth-doped Si–ZrO_2 co-sputtered films

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Abstract

Er-doped Si-yttria-stabilized zirconia (YSZ) thin film samples were prepared by rf co-sputtering. Chemical composition of the samples was determined using energy-dispersive spectroscopy (EDS) and the structure of the films by X-ray diffraction (XRD). The samples were annealed to 700 °C. Photoluminescence (PL) measurements were performed for the visible and infrared. By exciting with the 488-nm-laser line the Er^{3+} emissions $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, $^4F_{9/2} \rightarrow {}^4I_{15/2}$ and a narrow $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission were observed. The $^4I_{11/2} \rightarrow {}^4I_{15/2}$ emissions for the same excitation wavelength were weak. Excitation wavelength dependence of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emissions indicated that the emissions were due to a combination of energy transfer from Si nanoparticles (np) to Er ions and energy transfer from defects in the matrix to the Er ions for excitations resonant with the energy levels of such defects. $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission decay measurements show two decaying populations of Er ions according to their locations with respect to other ions or any non-radiative defects. $^4I_{11/2} \rightarrow {}^4I_{15/2}$ emission dependence on $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission showed that the former was possibly due to a combination of downconversion from higher levels of the Er ions, energy transfer from Si nanoparticles and upconversion transfer processes. We concluded that Er-doped Si-YSZ is a promising material for photonic applications being easily broadband excited using low-pumping powers.

Keywords: Photoluminescence; Erbium; Yttria-stabilized zirconia; Silicon nanoparticles

1. Introduction

Zirconium oxide has been proposed as an excellent material for optical applications due to its hardness, high optical transparency in the 0.3–8 μm range, and high refractive index [1,2]. With a wide optical bandgap of 5.22–5.8 eV [3], that reduces the probability of non-radiative decay, and with a low phonon energy (470 cm^{-1}), lower than that of SiO_2 (1100 cm^{-1}) and of Al_2O_3 (870 cm^{-1}) [4], that reduces the probability of phonon-assisted non-radiative relaxation, the number and probability of radiative transitions in rare earth-doped ZrO_2 increases, which has made such rare earth-doped oxides interesting for photonic applications. Luminescence in Pr^{3+}-, Tb^{3+}-, Eu^{3+}-, Sm^{3+}-, Er^{3+}-doped ZrO_2 (bulk, powders, nanocrystals or sol–gel) have been investigated [5–10]. Er-doped waveguides and LEDs have also been developed [11,12].

ZrO_2 crystallizes into three main phases: the monoclinic, tetragonal, and cubic. The monoclinic (*m*) phase is thermodynamically stable for temperatures below 1170 °C. From 1170 °C to 2370 °C ZrO_2 is tetragonal (*t*), while above 2370 °C ZrO_2 is cubic (*c*) until it melts at 2706 °C [13]. The tetragonal phase is stabilized at relatively low temperatures by the addition of dopants such as Er^{3+}, Y^{3+}, and Ca^{2+} cations [4]. The cubic phase can be stabilized at low temperatures by addition of substitutional cations, such as Ca^{2+}, Mg^{2+}, and Y^{3+} [14]. Y_2O_3 is used to stabilize the tetragonal (*t*) and cubic (*c*) phases of yttria-stabilized zirconia (YSZ) over the composition ranges 2–9 and 4–40 mol% of Y_2O_3. The Y^{3+} dopants substitute for the host cations and to preserve charge neutrality, one O vacancy V^0 must be created for each pair of dopant cations. In YSZ local atomic environments differ from stoichiometric high temperature *t*- and *c*-phases of pure ZrO_2 due to the presence of relaxed defects. The average cation

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coordination number (7–8) is reduced gradually with increasing Y_2O_3 [15]. YSZ ($(ZrO_2)_{1-x}(Y_2O_3)_x$) has the CaF_2 cubic structure for a wide range of values of x. Oxygen vacancies result in the departures from the fluorite-type lattice. Oxygen coordination around active impurities can be sixfold, sevenfold or eightfold for Eu^{3+}- and Er^{3+}-doped YSZ [16].

Er-doped silicon-rich silicon oxide (SRSO) films present IR photoluminescence (PL) at the 1.54 μm emission with the advantage of being able to be pumped with low power sources, including inexpensive visible laser diodes and broadband sources such as visible LEDs [17,18]. The high absorption cross-sections and broadband absorption in the visible range of the Si nanoparticles (np) allow them to be efficient sensitizers to enhance the Er^{3+} 1.54 μm emission [17–19]. It is then of great interest to investigate the spectroscopic properties of Si np-sensitized Er^{3+} emissions in YSZ films for photonic applications.

2. Experimental

Er_2O_3–Si–YSZ film samples were prepared by non-reactive co-sputtering. The YSZ target (ZrO_2 + 12 wt% Y_2O_3) has an area of 181.46 cm^2. The Er_2O_3 target area used was 1.43 cm^2; the Si target area used was 6.67 cm^2. The Er_2O_3/Si area ratio was 0.214 and the Si/YSZ area ratio was 0.037. The target–substrate distance is ~2.54 cm. The deposition time was 6 h and the deposition temperature ~125 °C. Fused silica substrates were used. The as-deposited long film denoted as ESYZO is 12.7 cm in length. Film chemical composition was determined along its length using a JEOL JSM-5800LV SEM equipped with EDAX®. Film thickness was measured for the as-deposited films using a Dektak Profilometer. The thickness of the film samples varies from 2 to 4 μm. The film samples were annealed to 700 °C for a 30 min stay, with a mean heating rate of 10.8 °C/min and a mean cooling rate of 2.4 °C/min. The film samples were characterized by X-ray diffraction (XRD) using a SIEMENS D-5000 equipment. PL measurements in the visible and the infrared were performed using an Ar laser, an ISA-TRIAX 320 spectrometer equipped with a Hamamatsu R2949 photomultiplier (PMT) and an InGaAs detector connected to a lock-in amplifier. Time decay measurements were performed using a Nd-YAG laser coupled to a MOPO producing an emission at 485 nm with pulse energy: 20 mJ, pulse width: 8 ns, repetition frequency: 10 Hz, and spot size: 2 mm. Measurements were performed using a SPEX 500 M 0.5 m monochromator equipped with a Hamamatsu R5108 PMT, a Ge detector and amplifier connected to a lock-in amplifier and a digital sampling oscilloscope.

3. Results and discussion

Chemical composition of the most representative film samples (labeled from F1 to F4) from long film ESYZO is shown in Table 1. For most of the film samples the Er content is relatively high, being close to 1.0 at% (10,000 ppm). The Er content in most commercial-doped fibers does not exceed 1000 ppm to avoid concentration-quenching effects [20]. XRD patterns for the film samples presented in Table 1 annealed to 700 °C are presented in Fig. 1. The peaks or bands labeled with asterisks correspond to the fused silica substrate and were identified as such after comparing several Er-, Nd-doped and undoped Si-rich oxide (SiO_2, Al-SiO_2, Al_2O_3, and YSZ) films all deposited on fused silica substrates. The peaks that correspond to the Er-doped Si-rich YSZ films were identified as being of crystalline ZrO_2 phases (tetragonal (*t*-), cubic (*c*-), and monoclinic (*m*-)). The cubic phase seems to be predominant for the samples with highest Zr and Y contents, but its presence decreases appreciably as both the Zr and Y contents decrease. The monoclinc phase seems to increase its presence as the Zr and Y contents decrease. The tetragonal phase presents a change in grain orientation with the decrease in both Zr and Y content. The XRD patterns for the as-deposited films (not shown) indicate that the Y_2O_3 molar percentage (6.9 mole%) of the YSZ target allows for the stabilization of the *t*-ZrO_2 and *c*-ZrO_2 phases upon deposition. The relative oxygen deficiency with higher Zr and Y contents could be the reason for the segregation of the crystalline phases. The overall relative oxygen deficiency in the film samples suggests high presence of oxygen related vacancies within the film. Then the structure of the film samples depends mostly on the variation of the Zr, Y, and O contents.

Table 1
Chemical composition of long film ESYZO

Film sample reference	Zr (at%)	Y (at%)	O (at%)	Si (at%)	Er (at%)
F1	32.91	4.35	58.37	3.52	0.85
F2	31.27	4.05	60.18	3.65	0.85
F3	31.79	4.00	59.05	4.09	1.07
F4	30.08	3.89	58.42	6.98	0.63

Representative visible PL spectra of the film samples of ESYZO can be seen in Fig. 2. The spectra of the as-deposited film sample F3 for 488.0 nm excitation at 20 mW and of F3 annealed to 700 °C for 457.9 and 488.0 nm excitations at 20 mW are shown in Fig. 2. Fig. 3 shows possible components that could make up the visible PL spectra of the film samples for 488.0 nm excitation, including emissions related to oxygen vacancy defects or interstitial oxygen defects [2,14,21,22] in ZrO_2 or YSZ, Si=O surface state emissions [23] related to small SiO_x ($x<2$) regions within the film samples and the following Er^{3+} emissions: $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, which correspond to downconversion PL. Interference patterns are observed in the visible PL spectra for the film samples annealed to 700 °C due to change in the refractive index with annealing. For 457.9 nm excitation the Er^{3+} emissions are not present in the visible PL spectra.