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Luminescence properties of Sm³⁺-doped polycrystalline ZrO₂

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ABSTRACT

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Keywords: Optical properties Luminescence We obtained samarium-doped zirconia using two different routes. In one, atomic layer deposited thin crystalline films were doped by using ion implantation; this sample was mainly monoclinic. The other method, the skull-melting technique, yielded polycrystalline bulk zirconia containing both monoclinic and tetragonal phases of ZrO₂. Thorough photoluminescence (PL) measurements of Sm emission in these materials were performed using pulsed laser excitation at 405, 320 and 230 nm, respectively corresponding to direct, defect-related and host-sensitized excitation. Both samples exhibited well-resolved emission series of Sm³⁺. In general, the recorded spectra may be considered as superpositions of two different sets of lines attributable to Sm³⁺ centers in different crystalline phases of ZrO₂. These results have been confirmed by time-resolved measurements, which also suggest that all emission lines originate from a common initial state (${}^4G_{5/2}$) with a lifetime of about 1 ms. As expected, the host-mediated excitation leads to a prolonged decay profile attributed to the retarded energy transfer from host to guest. © 2008 Elsevier B.V. All rights reserved.

1. Introduction

ZrO₂ is an attractive material for optical applications. Its good transparency up to vacuum ultraviolet, high refractive index, superior mechanical strength and high optical damage threshold render the material particularly suitable for optical coatings and waveguides. Additionally, ZrO₂ has been proposed as a prospective scintillator, due to its high density and efficient VUV excitation [1]. However, the intrinsic emission of zirconia is quite weak at room temperature and notably sensitive to the quality of material. Therefore, more robust emission centers, e.g. rare earth (RE) impurities, must be introduced to be efficiently excited through the energy transfer from the host. The wide band-gap of ZrO_2 (~5 eV) enables RE emission in the visible range, whereas the low phonon energies of the matrix ($<650 \text{ cm}^{-1}$) suggest a high yield of luminescence (low multiphonon relaxation). RE doping is also necessary to implement active waveguides. Moreover, it has been found that electrical conduction of samarium-doped zirconia is predominantly ionic below 600 °C and thus a potential material for some types of fuel cells [2].

Successful samarium activation of the matrix has been reported by a number of authors [3–6], mainly using the sol–gel approach for preparation. Both monoclinic and (impurity-stabilized) tetragonal phases of zirconia have been reported, though the phase content's manifestation in the fine structure of Sm emission has not

* Corresponding author. E-mail address: sven.lange@mail.ee (S. Lange). been clearly indicated. Furthermore, a discrepancy seems to exist in the emission lines' assignment. Below, we report the spectroscopic results of using two different routes for preparation of Sm-doped ZrO₂: atomic layer deposition (ALD) with ion implantation and a skull-melting technique (SMT). ALD is able to produce uniform films of controllable thickness (even on profiled surfaces) whereas SMT yields a high-quality bulk material.

2. Experimental

Thin films were grown by using chloride-based ALD processes. The films were deposited on single-crystal (100)-oriented Si substrates in a low-pressure ALD reactor [7]. The films were 250 nm in thickness, as evidenced by reflection spectra. According to XRD and RHEED studies, the samples were mainly monoclinic and contained small amounts of the tetragonal phase.

The doping of ALD-grown films was achieved by implantation with Sm³⁺ ions at room temperature. Ion energy of 300 keV was chosen in order to obtain an ion distribution profile centered approximately in the middle of the film. The estimated impurity concentration averaged over the film's thickness was 1.4×10^{-3} at.%. Annealing of the implanted samples was required to observe emission of incorporated RE ions. Annealing in air was performed up to 1000 °C, leading to near-maximum intensity of Sm³⁺ emission.

Crystals of ZrO_2 containing 4 mol% of Sm_2O_3 were grown by directional solidification of the melt using direct rf heating in a water-cooled crucible (SMT) [8]. The growth rate was 10 mm/h.



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The cooling rate of the crystal was 180–200 °C/min at temperatures above 1000 °C and 30 °C/min in the 1000–500 °C temperature range. The obtained crystals were more or less opaque (milky), depending on the amount of stabilizer, and light orange– yellow in color. The XRD study has indicated the presence of nearly equal amounts of monoclinic and tetragonal phases (see Ref. [8] for in-depth description). The significant content of the tetragonal phase is attributable to the stabilizing effect of Sm impurities.

PL measurements were performed at room temperature in the backscattering configuration. A pulsed (10 ns pulse width, 20 Hz repetition rate) tunable OPO laser was used as the excitation source at various wavelengths (405, 320, and 230 nm). The emission spectra were recorded using a spectrograph (Andor SR-303i) equipped with an air-cooled ICCD detector (Andor DH501) permitting time-resolved measurements. The decay kinetics of Sm emission was recorded using a photon counting system consisting of a photomultiplier tube (Hamamatsu H8259-01) and a multichannel analyzer (FAST ComTec P7882).

3. Results

Emission spectra characteristic for Sm³⁺ ions were recorded under photoexcitation at various wavelengths (see Fig. 1). A well-resolved fine structure was observed due to the Stark splitting of free-ion energy levels in the crystal field. This indicates the presence of well-defined crystal sites for the impurity ions. However, marked differences between the fine structures are noticeable depending on the sample's type and the excitation wavelength.

In the case of the ALD-grown sample shown in Fig. 1, the emission was recorded only under band-to-band excitation of the host, due to the low concentration of impurities and thinness of the film. The emission spectrum was identical to that reported previously [3,5,6]. We could identify at least 16 Stark components with wavelengths of 563.5, 571.5, 600, 609, 616, 620, 623, 627.5, 648.5, 651, 658, 661, 666, 670.5, 714 and 718.5 nm.

However, excitation of the SMT-grown sample shown in Fig. 1 as lines b–d leads to the appearance of an additional set of spectral lines identified as the wavelengths of 575.5, 577, 593.5, 607.5, 624, 668, 674 and 721.5 nm. In general, a superposition of the two sets



Fig. 1. PL spectra of Sm³⁺-doped ZrO₂, ALD-grown (a) and SMT-grown (b–d). Lines attributed to the tetragonal phase indicated with vertical dotted lines.



Wavelength $\lambda(nm)$

Fig. 2. Time-resolved spectra of SMT-grown ZrO_2 : Sm^{3+} sample excited at various wavelengths. Time windows of $1-6 \ \mu s$ shown as dotted lines, $1-11 \ ms$ – solid lines.



Fig. 3. Luminescence decay curves excited at various wavelengths. Emission detected at 620 nm ($\Delta\lambda$ = 1.1 nm).

of spectral lines was observed in this sample, the ratio depending on the excitation wavelength.

Time-resolved measurements were performed to clarify the situation further. The obtained time-resolved spectra (see Fig. 2) indicate that the decay rates of individual spectral lines are nearly identical in each set. In the case of 230 nm excitation, the first set of spectral lines in the spectrum obtained by integrating emission within $1-6 \mu$ s after the laser pulse is the strongest. At significantly longer timescales (1-11 ms), the second set of spectral lines prevails.

The decay of Sm³⁺ emission at various excitation wavelengths is presented in Fig. 3. A clear difference between excitation at 230 nm and longer wavelengths is noticeable: the decay kinetics of the emission excited at 230 nm contains a prominent prolonged tail.

4. Discussion

According to XRD measurements, the ALD-grown sample contains mainly the monoclinic phase. Therefore, the first set of spectral lines (a in Fig. 1) must be considered to originate from Sm³⁺ centers in the monoclinic structure of ZrO₂. Although ZrO₂ samples of various phase content have been investigated, only these spectral lines have been reported [3,5,6]. The additional spectral lines observable in the SMT-grown sample are probably due to Sm³⁺ centers in the tetragonal phase, a conclusion supported by an earlier report on the PL spectrum of Sm³⁺ in a substantially tetragonal phase of ZrO₂ [9].

The time-resolved spectra indicate common decay rates of the individual Stark components in each set, suggesting a common initial state (apparently ${}^{4}G_{5/2}$). Indeed, as the energetic spacing between ${}^{4}F_{3/2}$, ${}^{4}G_{7/2}$ and ${}^{4}G_{5/2}$ is around 1100 cm⁻¹, the highest phonon frequency of ZrO₂ (650 cm⁻¹) should be sufficient for relaxation of ${}^{4}F_{3/2}$, ${}^{4}G_{7/2}$ to the lowest ${}^{4}G_{5/2}$ manifold [10]. These considerations question earlier conclusions [6].

Different excitation wavelengths lead to different intensities, different spectra and different decay curves of the SMT-grown sample, indicating complicated and phase-dependent excitation and relaxation processes. Considering the previously reported excitation spectrum of Sm^{3+} in ZrO₂ [3] and other crystals, we can assign 405 nm to the direct excitation of Sm^{3+} ions. However, it remains to be explained why the excitation of ions in the tetragonal phase is prevalent, as shown in Fig. 1.

Much more efficient excitation at 230 nm corresponds to the excitonic peak just below the band edge of monoclinic ZrO_2 [1,11]. The PL spectrum contains emission lines corresponding to both phases of ZrO_2 . An essential indication of host-mediated excitation has been observed in the decay profile containing a prominent prolonged tail exceeding by far the natural lifetime of an excited Sm³⁺ ion (in the 1 ms range, see Fig. 3). This prolonged decay is attributable to the retarded energy transfer from the host due to diffusive migration or a tunneling recombination of trapped charge carriers [12].

It is more difficult to explain the excitation route of the 320 nm excitation. While the emission spectrum, intensity and decay are similar to those of the 405 nm excitation, the decay curve contains a weak but noticeable tail. Sm³⁺ has no considerable absorption in this range. It might be related to a defect state of tetragonal ZrO₂ and requires further investigation. Notably, a wide excitation band

of Sm³⁺ in monoclinic ZrO₂ around 310 nm has been reported previously [5].

5. Conclusions

The study of the fine structure in the (time-resolved) luminescence spectra of Sm^{3+} ions in ZrO_2 revealed the existence of at least two different luminescence centers connected with monoclinic and tetragonal phases of ZrO_2 . Excitation at 405 nm leads to the direct excitation of Sm^{3+} , whereas the efficient excitation at 230 nm is considered host-sensitized excitation (probably via excitonic state), as suggested by the emission decay profiles.

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