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Influence of annealing temperature on the electron–lattice coupling strength in terbium doped yttrium alumina perovskite xerogels embedded in nano-porous anodic alumina

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ABSTRACT

Terbium doped $YAlO_3$ xerogels were synthesized and spin-coated onto porous anodic alumina substrates. After deposition the films were annealed at temperatures between 400 and 1000 °C. The influence of the annealing temperature on terbium emission and the terbium excitation mechanism were investigated by means of photoluminescence, photoluminescence decay and photoluminescence excitation spectroscopy. It was found that both photoluminescence lifetime and the energy difference between spin-forbidden and spin-allowed 4f–5d transitions decreases with the annealing temperature drop. This dependence was correlated to the electron–lattice coupling strength calculated as a function of annealing temperature.

1. Introduction

The development of a sol–gel technology used for the fabrication of advanced light-emitting materials has received considerable attention due to the cost-efficiency of the method as well as the ability to adjust the structural and physical properties of the material. The sol–gel technology allows for the fabrication of solid films from liquid colloidal solutions, particularly xerogels doped with various lanthanide (Ln^{3+}) ions. Significantly, sols with a low viscosity can penetrate the mesoscopic channels of porous silicon, artificial opals, porous anodic alumina and other porous materials, resulting in a xerogel formation inside the pore volume [1].

Among various porous materials, porous anodic alumina (PAA) has received growing interest due to low fabrication cost, optical transparency in the visible and infrared ranges as well as mechanical and thermal durability. PAA is known to exhibit regular pore morphology, with the pores placed at the center of approximately hexagonal cells whose size can be adjusted [2]. Moreover, due to the structural regularity of the pores, PAA can be considered as a two-dimensional photonic crystal [3,4]. In PAA, photon density of states (DOS) is redistributed over a solid angle to give maximum DOS along pore axes (direction of high transmission) and minimal DOS within the plane normal to pore axes (direction of high reflection) [5]. This effect could be used to enhance light propagation along the axes parallel to the pores. In this way, if the channels of PAA were filled with a lanthanide doped xerogel emitting light at a certain wavelength, highly directional, multicolor luminescent images could be obtained [6]. Recently, applications of PAA for LCD panel displays have been proposed [7]. However, in order to put these ideas into practice, one must examine the optical properties of a sol–gel material placed inside of the PAA pores. In this work we examine PAA structures filled with Tb-doped $YAlO_3$ xerogel (green light emitter). The main aim of this study is to explain excitation and emission mechanism of Tb ions in these structures and to find factors limiting the radiative recombination of Tb.

Among various factors affecting the optical properties of Ln^{3+}-doped materials, the host-matrix crystal structure and the Ln^{3+} local environment are the most important. Depending on the Ln^{3+} ion environment, the oscillator strength of $4f \leftrightarrow 4f$ and $4f \leftrightarrow 5d$ transitions could be influenced [8], leading to significant changes of the structure emission and absorption properties. Moreover, the structural environment of the ion may affect the electron–lattice coupling strength [9]. This is also an important issue, since in the case of a strong electron–lattice coupling an efficient multiphonon relaxation of the excited ion occurs [10], limiting light output from a hypothetical device. In our experiment, the structural properties (e.g. the xerogel crystallinity) can be controlled by depositing a set of samples annealed at various temperatures

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[11]. In this study, we synthesized terbium (Tb^{3+}) doped $YAlO_3$ (YAP) xerogels, which were spin-coated onto PAA substrates and annealed at 400–1000 °C temperature range. The pores morphology was kept constant for all the samples. The optical properties of these structures were then experimentally examined by means of photoluminescence, time-resolved photoluminescence and temperature-dependent photoluminescence excitation spectroscopy. We showed that both emission and absorption properties are strongly influenced by the annealing. This effect was ascribed to changes of the local Ln^{3+} environment, which was also found to affect the electron–phonon coupling strength for the dominant spin allowed $4f^8 \rightarrow 5d_14f^7$ transition of Tb. We have shown that this transition strongly couples to lattice vibrational modes and the coupling strength increases with the annealing temperature drop.

2. Experimental

A super-pure aluminum was magnetron-sputtered onto a planar side of a polished wafer of monocrystalline silicon. Aluminum was completely anodized in a 1.2 M orthophosphoric acid solution at a constant temperature of 17 °C and a constant voltage of 130 V. As obtained from scanning electron microscopy, the PAA thickness was equal to 9 μm, and the average pore diameter was equal to 140 nm. Terbium doped yttrium-alumina oxides were prepared by stage-by-stage dissolution of nitrate salts (Sigma–Aldrich) $Y(NO_3)_3{\cdot}4H2O$ (99.99% purity), $Al(NO_3)_3{\cdot}9H_2O$ (98% purity) and $Tb(NO_3)_3{\cdot}5H_2O$ (99.9% purity) in an aqueous-alcoholic solution, with pH adjusted to 2 with diluted nitric acid. As a stabilizer, citric acid in the molar ratio [metal ions]/[citric acid] = 1/3 was used. Terbium-containing solution was deposited on PAA templates by sequential spinning at a rate of 2700 rpm, followed by drying at 200 °C, and a final 30 min. annealing at temperatures of 400, 900 and 1000 °C (under air). The determined Tb concentration in the samples is 3.95 at.%. Moreover, as it was shown by X-ray diffraction [12], matrix annealed at T_a = 400 °C is completely amorphous. For T_a = 900 °C and T_a = 1000 °C matrix crystallizes and $YAlO_3$ phase is formed with a small admixture of Al_2O_3 phase as well. It should also be emphasized that the structural parameters of PAA templates (e.g. pore size, pore density and pore depth) were kept constant for all of the spin-coated samples. This allowed for a qualitative comparison of the optical properties between the samples annealed at different temperatures, without considering the influence which the pores may have on light generation or light propagation in the structures. Moreover, as determined by a cross-sectional SEM experiment, the fill-factor of the pores is about 25% and the filling is non-uniform (the pores are not completely filled out).

For photoluminescence (PL) and photoluminescence excitation (PLE) a xenon lamp (450 W) connected to a monochromator (Jobin Yvon TRIAX 180) was used as the excitation source. PL and PLE signals were collected by an optical fiber coupled to the CCD camera (HR4000 Ocean Optics). In the case of the PLE, the obtained signals were divided by the light source spectral intensity profile. The PLE measurements were performed as a function of temperature in the 10–300 K range (spectra were collected every 10 K), using closed-cycle (helium) cooler. The flash xenon lamp and PMT detector coupled with monochromators (Photon Technology International) were used for PL decay measurements.

3. Results and discussion

The low temperature (T = 10 K) PL spectra of YAP:Tb^{3+}/PAA structures obtained for λ_{EXC} = 270 nm excitation wavelength (4.59 eV) are shown in Fig. 1 as a function of the annealing temperature T_a (for T_a equal to 400, 900 and 1000 °C). For each sample,

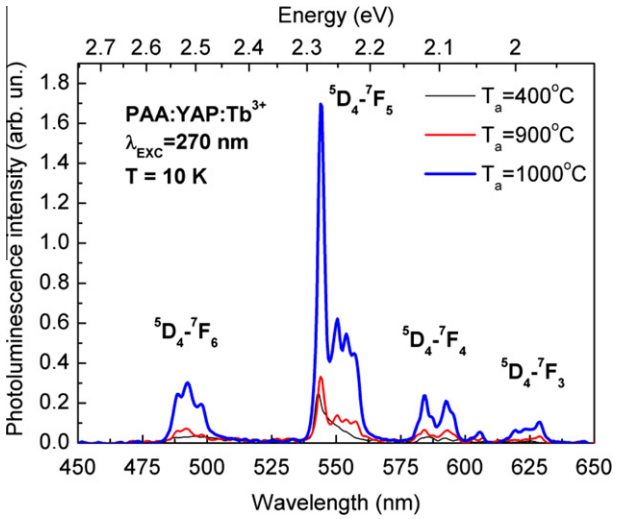

Fig. 1. Photoluminescence spectra measured at low temperature (T = 10 K) for samples annealed at 400, 900 and 1000 °C.

four main PL bands can be seen that originate from radiative transitions between Stark-split intra-4f energy levels of Tb^{3+} ions. The observed transitions are $^5D_4$–$^7F_6$ (492 nm), $^5D_4$–$^7F_5$ (544 nm), $^5D_4$–$^7F_4$ (587 nm) and $^5D_4$–$^7F_3$ (625 nm) [13], with $^5D_4$–$^7F_5$ transition being the most intensive. Fig. 1 also shows that rise of the annealing temperature results in significant enhancement of the PL intensity. As it was shown in our previous paper [12], for T_a = 400 °C the matrix is completely amorphous whereas for T_a = 900 °C and T_a = 1000 °C crystallization occurs and $YAlO_3$ polycrystalline phase is formed inside the anodic alumina pores, with small admixture of Al_2O_3 phase. Thus, the crystalline quality of the matrix is closely correlated to the emission intensity of the structures.

Fig. 2 shows photoluminescence excitation (PLE) spectra obtained as a function of temperature (only 10 K, 150 K and 300 K are shown for clarity reasons) for samples annealed at 1000, 900 and 400 °C. The PLE spectra were obtained by integrating the narrow emission line at 544 nm (2.28 eV) for each excitation wavelength. In general, three main excitation bands can be seen, centered at around 3.8, 4.6 and 5.3 eV. The bands position changes slightly from sample to sample. The 3.8 eV and 4.6 eV bands may be attributed to forbidden high-spin ($5d_1$HS) and allowed low-spin ($5d_1$LS) $4f^8 \rightarrow 5d_14f^7$ transitions [14], respectively ($5d_i$ denotes the i-th 5d energy level, in order of increasing energy). Furthermore, the 5.3 eV band may be attributed to the allowed low-spin ($5d_2$LS) $4f \rightarrow 5d_2$ transition. Similar excitation bands have been observed earlier [15]. It can be thus concluded that in the investigated structures the most effective excitation mechanism is through f–d transitions.

The relative intensity of the observed excitation bands significantly changes as a function of the annealing temperature. Especially, the intensity ratio I_{HS}/I_{LS} between the $5d_1$HS and $5d_1$LS absorption bands increases as the annealing temperature decreases, being equal to 0.01, 0.28 and 1.76 for 1000, 900 and 400 °C, respectively. Partially, this effect could be related to mixing the 5d orbital with anion ligand orbitals that reduces the spin purity of the state. As a result, the oscillator strength of the spin forbidden transition relative to that of the spin allowed transition increases. This effect is known to significantly influence the I_{HS}/I_{LS} ratio. However, it must be emphasized that the interpretation of PLE results, especially the PLE intensities, is more complex than the interpretation of absorption results. In general, the PLE signal intensity, I_{PLE}, can be described as $I_{PLE} \sim P_{abs}P_{rel}P_{em}$ [16], where P_{abs},