Thin Solid Films 553 (2014) 13–16

Contents lists available at ScienceDirect

Thin Solid Films

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

Optical properties of rare earth-doped TiO_2 anatase and rutile thin films grown by pulsed-laser deposition

E. Le Boulbar [a], E. Millon [a,*], C. Boulmer-Leborgne [a], C. Cachoncinlle [a], B. Hakim [b], E. Ntsoenzok [b]

[a] GREMI, UMR 7344 CNRS-Université d'Orléans, 45067 Orléans Cedex 2, France
[b] CEMHTI, UPR 3079 CNRS, 1D Avenue de la Recherche Scientifique, 45071 Orléans, France

ARTICLE INFO

Available online 18 November 2013

Keywords:
Titanium oxide
Rare earth
Energy transfer
Photoluminescence
Down shifting
Solar cell
Photovoltaic
Pulsed-laser deposition

ABSTRACT

Ln^{3+} (Ln = Tm, Eu and Yb) doped titanium dioxide anatase and rutile films have been grown by pulsed-laser deposition at 700 °C under 0.1 mbar O_2. By using c-cut (0001) Al_2O_3 sapphire or (100) $LaAlO_3$ single crystal substrates, TiO_2 films doped with Ln^{3+} are constituted with either highly oriented (200) rutile or (004) anatase, respectively. Energy transfer from TiO_2 to Ln^{3+} is studied by photoluminescence spectroscopy with UV excitation (364 nm) under band gap excitation of the oxide matrix. It is demonstrated that Tm^{3+} dopant is not efficient as sensitizers. On the contrary, energy transfer from TiO_2 to Eu^{3+} and Yb^{3+} occurs in both matrixes, which make this material suitable for down-shifting purpose. Results obtained for Yb^{3+} compared with our previous study on Nd^{3+} show that Nd^{3+} doped-rutile and Yb^{3+} doped-anatase are the more efficient combinations to convert UV to NIR photon. Finally, a cooperative conversion mechanism is suggested to explain the higher integrated photoluminescence intensity found in anatase Yb^{3+} rather than in rutile.

1. Introduction

Enhancement of silicon solar cell yield by using spectral shifting, is of great interest since the calculation of Trupke et al. predicted an efficiency up to 39% from down- and up-conversion process [1]. Owing to the various mechanisms used to convert photon energy [2], inorganic oxide host doped with rare earth (RE) elements for down shifting (DS) or codoped RE system for down conversion (DC) has been extensively studied. B.S. Richards pointed out that TiO_2 could be an appropriate matrix for DC or DS because its high-refractive index (3.5) and its excellent transparency to visible/NIR light and its low cut-off frequency phonon (826–600 cm^{-1}) are suitable to silicon solar cell technology requirements [3]. However, an efficient energy transfer from the matrix to sensitizer has to occur to achieve a spectral emission in the NIR range. The wide bandgap oxide semiconductors ZnO and TiO_2 have been widely used as host matrix for RE doping: for example NIR luminescence has been evidenced in ZnO doped by Yb^{3+} [4], Nd^{3+} [5] or in TiO_2 doped with Sm^{3+}, Eu^{3+}, Yb^{3+}, Er^{3+} [6] or Nd^{3+} [6,7]. In such systems, the energy transfer is demonstrated through PL emission from excitation in the UV range of the oxide matrix compared with that obtained by direct excitation of the RE element. Recently, the effect of the structural properties of TiO_2 matrixes on Nd^{3+} emission has been investigated through photoluminescence (PL) spectroscopy measurements: it has been showed that highly crystalline rutile matrix doped with 1 at.% Nd^{3+} is suitable to obtain intense PL emission of the RE and efficient matrixes to RE energy transfer [8].

In this paper, the PL properties of Ln^{3+} (Ln^{3+} = Tm^{3+}, Eu^{3+}, and Yb^{3+}) have been recorded upon excitation of TiO_2 band gap in order to investigate matrix to Ln^{3+} energy transfer depending on the nature of the TiO_2 phase as host matrixes. For this purpose, well-crystallised, oriented and singled-phase TiO_2 anatase or rutile films doped with RE ions, have been grown by using the pulsed-laser deposition (PLD) method which is well suitable to grow high crystalline quality thin films with complex composition for various applications [9–11]. Indeed, the nature of TiO_2 phases and their main axis growth can be adjusted by choosing appropriate transparent substrates as $LaAlO_3$ (100), and Al_2O_3 (0001) [12–14]. The luminescence of the TiO_2:Ln^{3+} has been therefore recorded in both anatase (labelled A-TiO_2 in this paper) and rutile (R-TiO_2) based. Possible energy transfer mechanisms occurring in anatase and rutile host matrix are suggested to explain energy transfer differences in both matrixes.

2. Experimental details

Ln^{3+} doped-TiO_2 thin films were grown by PLD with a KrF Lambda Physics Compex 201 laser (wavelength: 248 nm, pulse duration: 27 ns, repetition rate: 20 Hz). The experimental set-up was described elsewhere [15]. Depositions were performed onto c-cut sapphire and (100) $LaAlO_3$ single crystal substrates. The laser beam was focused onto the target (focusing diameter: 1.5 mm) with a fluence of 4 $J \cdot cm^{-2}$ under a 45° incident angle. One inch TiO_2 targets doped with around 1% at. Ln^{3+} concentration were used for the experiments. Oxygen gas was introduced into the ablation chamber with a mass flow controller to maintain the desired partial pressure (10^{-1} mbar–10 Pa). Substrates were heated at 700 °C, the deposition process being initiated when the

* Corresponding author.
E-mail address: eric.millon@univ-orleans.fr (E. Millon).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.11.032

temperature is stabilised. After deposition, the substrate was held at 700 °C for 10 min, and then cooled at room temperature after switching off the electrical supply of the substrate holder.

The thickness and composition of the titanium oxide based-films were measured by Rutherford backscattering spectrometry (RBS), using a 2 MeV energy $^4He^{2+}$ ion beams from the Van de Graaff accelerator of the SAFIR IBA laboratory, Université Pierre et Marie Curie, Paris, France. By using the RUMP simulation programme, the precise determination of the in-depth distribution of the elements of films and substrates was obtained. The structural characterizations of the titanium oxide films were carried out by X-ray diffraction (XRD) analyses using a four circle diffractometer (Philips Xpert MRD) with the Cu K_α radiation ($\lambda = 0.154$ nm). Optical transmission measurements were performed on undoped rutile and anatase films grown on both side polished $LaAlO_3$ (100) and sapphire substrates using a spectrophotometer Jasco UV–Visible V-530, with a resolution of 2 nm, in 300 to 1000 nm wavelength range. PL emission spectra were recorded upon an UV excitation at 364 nm provided by a Spectra Physics argon laser. A Jobin-Yvon iHR320 spectrometer composed of a Czerny-Turner monochromator was used. InGaAs and photomultiplicator detectors were used to record PL intensity in the NIR and UV–Visible window, respectively. PL spectra were normalized according to film thickness, and a semi-quantitative comparison of PL yield is performed by taking into account the intensity of PL peaks related to RE^{3+} transitions.

3. Results and discussion

The RBS spectra (not presented here) show that the films are nearly stoichiometric with an O/Ti ratio equal to 2 whatever the substrate used. Such composition is classically observed on titanium oxide film grown under oxygen pressure (0.1 mbar–10 Pa) [12,13]. The structural properties have been investigated by XRD on undoped and Ln-doped TiO_2 films on the two substrates. Fig. 1 shows the typical XRD patterns of Ln-doped TiO_2 films. On (100) $LaAlO_3$ substrate, the peak located at $2\theta = 37.80°$, corresponds to a film with the anatase single phase oriented according to the (004) plane parallel to the surface substrate. The growth of films on (0001) Al_2O_3 substrate shows a main peak at $2\theta = 39.20°$, which is related to a rutile film with the (200) texturation. Such orientations depending on the used substrates are related to the possible epitaxial relationships between the film and the substrate as it has already been reported in our previous works [12,13]. It is worth noticing that the XRD diagrams of TiO_2 films doped by Ln^{3+}, show the same phases and orientations than those observed with undoped ones [12,13], and no peaks potentially related to impurity of other phases are observed. Nevertheless, a slight decrease of the crystallite size deduced from the full width at half maximum (FWHM) of the (200) and (004) diffraction peaks (Scherrer formula) may be observed for the RE-doped TiO_2 films in respect with that of undoped films. This is related to the structural disorder induced by the incorporation of RE dopant in such oxide matrix.

A typical UV–Visible transmission spectrum is presented in Fig. 2. The Ln-doped A-TiO_2 and R-TiO_2 samples show a transparency of about 90% and 80% in the visible range, respectively. The transmittance of doped-TiO_2 films is in the same order than that of undoped titanium oxide films. By using rather low dopant content (1%), it is therefore possible to preserve the intrinsic optical transmittance property of titanium dioxide. On the contrary, for higher doping amount (for example 5% Nd-doped TiO_2 film) it has been observed that the hybridization between 4f Nd and 3d Ti orbitals [16] or the 4f ➔ 4f Nd transition [17] would lead to a loss of transmittance at around 400–500 nm. Regarding the absorption edge, the optical bandgap of anatase-based films is shifted toward the shorter wavelength compared with the rutile-based films as generally observed in such films [18].

Tm^{3+} ions have been integrated in A-TiO_2 and R-TiO_2 in order to investigate matrix to Ln^{3+} energy transfer. PL measurements carried out on Tm^{3+}-doped TiO_2 host matrixes, show two peaks around 800 nm (Fig. 3). Around 800 nm, the peaks could be assigned to the theoretical transitions $^1G_4 \rightarrow {}^3H_5$. Others transitions theoretically located at 470 nm ($^1G_4 \rightarrow {}^3H_6$) and 650 nm ($^1G_4 \rightarrow {}^3F_6$) are not detected. It is therefore highly probable that energy transfer from matrixes to Tm^{3+} is due to a resonant process, which could arise from Ti^{3+} defect [6]. However, such energy transfer from TiO_2 to Tm^{3+} is too weak to achieve an efficient conversion process.

The PL spectra recorded for R- and A-TiO_2 films doped with 1 at.% Eu^{3+} (Fig. 3) demonstrate that energy transfer occurred under UV sensitization. Radiative desexcitation from level $^5D_0$ to ^7F_J (J = 1,2,3,4) of Eu^{3+} gives rise to four groups of peaks centred at 590, 615, 660 and 720 nm wavelengths in agreement with the emission levels involved for Eu^{3+} ion [19]. The PL intensity is twice larger in R-TiO_2 making such matrix interesting for DS purpose since a slight increase of silicon solar cell efficiency has already been demonstrated using Eu^{3+} [20].

R- and A-TiO_2 films doped with 0.7% at. Yb^{3+} sensitized by 364 nm gives rise to a group of peak from 970 to 1150 nm (Fig. 3). Only one transition is possible in Yb^{3+}, $^2F_{5/2} \rightarrow {}^2F_{7/2}$, leading to a centred emission at 980 nm. The apparition of multiplet and shoulder located after the principal emission at about 980 nm can be explained by crystalline field effect, which splits both levels into 3 and 4 distinct energy level. Yb^{3+} emission is around 5 times larger in A-TiO_2 matrix.

In the same way, the PL of TiO_2 film doped with 1% at. Nd has been reported within rutile and anatase host matrixes [8]. As PL spectra were measured in the same condition and with the same detector, it is possible to compare integrated PL obtained for Yb^{3+} and Nd^{3+}. Fig. 4 shows the integrated PL intensity from 800 to 1200 nm for both Yb^{3+} and Nd^{3+} in A-TiO_2 and R-TiO_2 matrixes. Energy transfer is found to be

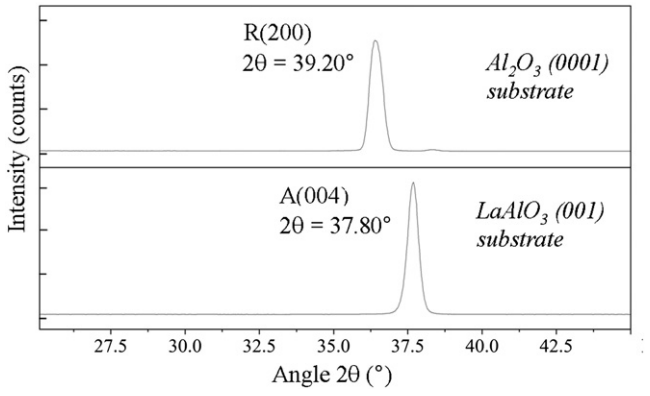

Fig. 1. Typical θ/2θ XRD patterns of RE^{3+}-doped TiO_2 thin films grown on c-cut (0001) sapphire, and (100) $LaAlO_3$ substrates at 700 °C under 0.1 mbar (10 Pa) in O_2. The diagrams shown here correspond to TiO_2 films doped with 1% Nd.

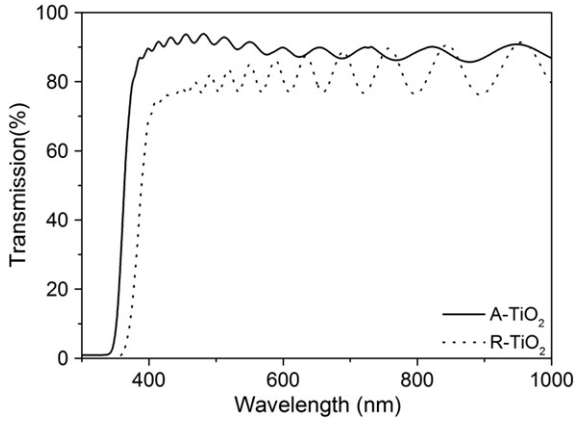

Fig. 2. Typical transmission spectra of RE^{3+}-doped R-TiO_2 and A-TiO_2 films grown at 700 °C under 0.1 mbar (10 Pa) in O_2 on c-cut (0001) sapphire, and (100) $LaAlO_3$ substrates, respectively. The spectra shown here correspond to TiO_2 films doped with 1% Nd.