Abstract

The structure and the luminescence properties of neodymium- and terbium-doped SnO$_2$ thin films were investigated by using x-ray diffraction and electron microscopy, infrared absorption, Raman and photoluminescence (PL) spectroscopies. The films were obtained by evaporation of SnO$_2$ and rare earths (RE) on silicon substrates maintained at 100°C. The as-deposited films were sub-stoichiometric and the films were then annealed in air at different temperatures. The structural characterization shows that the rutile phase is obtained for annealing temperatures greater than 600°C. In this phase, photoluminescence experiments show that the rare-earth ions are optically activated.

1. Introduction

The down-conversion process consists in converting one photon in one (down-shifting) or two (quantum cutting) photons with lower energy. Such mechanism can be used to increase the efficiency of the next generation solar cell by conversion of ultraviolet photons in lower energy ones, better absorbed by the Si-based photovoltaic cells [1]. These conversion layers can be obtained by doping transparent and conductive oxide (TCO) layers used as electrodes in solar cells with rare earths ions.

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The light emission from the RE generally arises from intrashell transitions of $4f$ electrons which are electric dipole forbidden at least for isolated ions. Hence, a resonant excitation of the RE leads to a weak luminescence efficiency. However, an indirect excitation mechanism can lead to a strong increase of the excitation efficiency of the optically active ions.

Among the rare earth elements, neodymium presents several technologically important luminescent bands including the $4F_{3/2} \rightarrow 4I_{11/2}$, $4F_{3/2} \rightarrow 4I_{9/2}$ and $4F_{3/2} \rightarrow 4I_{13/2}$ 4$f$-shell transitions which are, respectively, the basis of 1050 nm Nd lasers, a second lasing transition at 900 nm, and a 1300–1400 nm band in the second fiber transparency window. The transitions at 900 nm and 1000 nm also render Nd$^{3+}$ ions of particular interest for silicon based solar cells [2].

Terbium is interesting in optoelectronics for its green luminescence emission at around 545 nm. Tb is also of prime interest for solar applications due to its excitation level at 484 nm. Indeed, doping materials with a couple of RE as terbium/ytterbium or terbium/erbium can lead to the quantum cutting effect [3].

In this paper, we present a study of the structure and the luminescence properties of undoped, Nd- and Tb-doped SnO$_2$ thin films by using x-ray diffraction, electron microscopy, infrared absorption, Raman and photoluminescence spectrosopies. We show that light emission of the rare earths can be obtained when the layers present the rutile structure.

2. Experimental

SnO$_2$ powder was evaporated from an electron beam gun in a high-vacuum chamber with a base pressure of 1x10$^{-9}$ mbar. During evaporation, a partial decomposition of the SnO$_2$ source occurred and the pressure increased until 1x10$^{-5}$ mbar. The silicon substrates were maintained at 100°C. The deposition rate of the oxide was controlled by a quartz microbalance and was equal to 0.1 nm/s. The layer thickness was 200 nm for all samples. The in-situ RE doping was performed from an effusion cell. The RE content, defined by C$_{RE}=[RE]/([Sn]+2[O]+[RE])$ was controlled by a quartz microbalance, with a relative error of ±5 %. Since the as-deposited samples were sub-stoichiometric, they were annealed in a tubular oven under air for one hour and at different temperatures up to 900°C.

The crystallographic structure was determined by grazing incidence X-ray diffraction (XRD) experiments carried out with Cu Kα (0.154 nm) incident radiation. A germanium crystal with an incidence angle of 1° was used as monochromator.

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were performed with a JEOL ARM200F microscope operating at an accelerating voltage of 200 kV to determine the average grain size of the thin films. For TEM-STEM observations, cross-sections of the samples were prepared by a conventional ion milling method after mechanical polishing.

The atomic bonding of the films was determined by Fourier transform infrared (FTIR) spectroscopy. The spectra were obtained in the 180-3000 cm$^{-1}$ range with a resolution of 8 cm$^{-1}$. The contribution of an uncoated reference silicon substrate was subtracted from the experimental spectra. Raman scattering spectra were acquired on a spectrometer equipped with a liquid nitrogen cooled CCD detector. The laser wavelength was the 488 nm emission line of an Ar$^+$ laser.

For the steady state photoluminescence experiments, the samples were excited by the 325 nm line of a 30 mW He-Cd laser. The PL signal was analyzed by a monochromator equipped with a 600 grooves/mm grating and by a photomultiplier tube. The spectral response of the detection system was precisely calibrated with a tungsten wire calibration source.

3. Results and discussion

Figure 1 shows the XRD patterns for the undoped samples as-deposited and annealed at different temperatures $T_a$. The as-deposited sample is amorphous, as demonstrated by the very large peak around 30°. For $T_a$ equal to 400°C, the spectrum shows narrow peaks which correspond to the tetragonal SnO phase with the lithium structure. When $T_a$ is raised at 700 and 900°C, the XRD results show the expected diffraction peaks from the tetragonal structure of the SnO$_2$ rutile-type cassiterite phase. For the intermediate annealing temperatures, between 500 and 600°C, peaks of the phases SnO and SnO$_2$ can be observed. For $T_a$ equal to 600°C, it is also possible to see the (003)
diffraction peak of the Sn$_3$O$_4$ phase at 33.7°. The evolution is similar for doped samples, which are amorphous after deposition and present the same diffraction peaks with increasing temperature up to 900°C.

Fig. 1. X-ray diffraction patterns of undoped SnO$_x$ films versus annealing temperature. The peak assignment is for SnO$_2$ for the top spectrum and SnO for the spectrum of the sample annealed at 400°C. The (003) diffraction peak of the Sn$_3$O$_4$ phase is presented for the sample annealed at 600°C.

Although the appearance of these different structures depend on the annealing temperature and duration, the heating rate, and the oxygen partial pressure, these results are in agreement with those of Pan et al. [4] who reported that evaporated films were amorphous when deposited at substrate temperatures below 300°C while films grown above 350°C have a crystalline $\alpha$-SnO structure. The structure of these films fully changes to the rutile phase when annealed at temperatures above 600°C. They also observe the (003) diffraction peak of the Sn$_3$O$_4$ phase. Lorentz et al. [5] observed also such an evolution with evaporated films which are amorphous at 100°C, which present the SnO phase at 200 and 300°C and the SnO$_2$ phase above 400°C.

Fig. 2. STEM image of an undoped film annealed at 700°C (a) and TEM image of a 2 at.% Tb-doped film annealed at 700°C (b).
TEM study was performed on undoped and Tb-doped samples. For example, Fig. 2 shows the STEM image of an undoped film annealed at 700°C and the TEM image of a 2 at.% Tb-doped film annealed at 700°C. Pure SnO$_2$ and Tb-doped SnO$_2$ films present grains with sizes around a few tens of nanometers. These values are a bit larger than the values obtained by Elouichet et al. [6] which observed SnO$_2$ grains with diameters ranging from 3 to 10 nm in Tb-doped samples annealed 20 min at 700°C. Doping does not seem to influence the grain size.

![Infrared absorption spectra of undoped SnO$_2$ films versus annealing temperature.](image)

Fig. 3. Infrared absorption spectra of undoped SnO$_2$ films versus annealing temperature.

Raman and infrared absorption spectroscopies can be used to differentiate SnO from SnO$_2$. The infrared absorption spectra for the undoped samples as-deposited and annealed at different temperatures are shown in Fig. 3 (similar results are obtained for doped samples). Since there is no peak in the high-wavenumber range, the spectra are only presented in the 180-700 cm$^{-1}$ range. The as-deposited sample, which has an amorphous structure, shows a large peak around 420 cm$^{-1}$ with a full width at half maximum (FWHM) equal to 100 cm$^{-1}$. The samples annealed at 300 and 500°C have the SnO structure and present a peak at 260 cm$^{-1}$ with a FWHM of about 50 cm$^{-1}$. For the sample annealed at 600 and 700°C which has the rutile-type structure of SnO$_2$, this peak can be deconvoluted into two peaks at 244 and 293 cm$^{-1}$ and other peaks appear at 467, 560 and 607 cm$^{-1}$. As explained by Hirata et al. [7], the peaks at 244, 293 and 607 cm$^{-1}$ correspond to E$_u$ modes and the peak at 477 cm$^{-1}$ corresponds to A$_{2u}$ modes in SnO$_2$. The origin of the peak at 560 cm$^{-1}$ is still unclear but has been attributed in literature to surface vibration modes [8].

![Raman spectra of undoped SnO$_2$ films versus annealing temperature.](image)

Fig. 4. Raman spectra of undoped SnO$_2$ films versus annealing temperature.
Raman spectrometry was also performed in order to characterize the vibration modes of the films (Fig. 4). Again, doped and undoped samples present similar results. For the amorphous as-deposited sample, only very weak peaks are observed. However, with samples annealed up to 500°C, peaks at 115 and 211 cm\(^{-1}\) were observed. They are attributed to the B\(_{1g}\) and A\(_{1g}\) modes, respectively, of the SnO structure [9]. For \(T_a\) equal to 600°C, peaks are observed at 145 and 170 cm\(^{-1}\). They can be attributed to the Sn\(_2\)O\(_3\) or Sn\(_3\)O\(_4\) phases [10]. For higher annealing temperatures, only a peak at 634 cm\(^{-1}\) (not presented on the figure) was observed for \(T_a\) equal to 900°C. This peak, with a very low intensity, corresponds to the A\(_{1g}\) mode of the SnO\(_2\) phase [9].

The photoluminescence of the films is visible with the naked eye, with a blue violet spot for the low annealing temperatures and a yellow orange spot for the higher annealing temperatures. Figure 5 shows the experimental spectra measured at room temperature. The as-deposited sample presents a weak band around 415 nm. Its intensity increases with the annealing temperature up to 500°C. With an annealing temperature above 600°C, a large band appears around 650 nm with a FWHM equal to 200 nm. The intensity of this band increases with \(T_a\), whereas the band around 415 nm remains practically unchanged.

Similar PL spectra were observed from sputtered films [11], from tin oxide nanowires and nanoribbons [12,13], and from nanoasterisks [14]. The large band around 650 nm was interpreted as a defect-related luminescence band, which could be due to oxygen vacancies and unoccupied electron states in the dangling bonds on the surface of SnO\(_2\) crystals. The peak centered at about 400 nm is due to the recombination of free excitons.
In order to understand better the origin of the PL bands, a study was performed as a function of the measurement temperature $T_m$ between room temperature and the liquid nitrogen temperature. The experimental spectra are presented in Fig. 6 for the sample annealed at 700°C. Whereas the band around 415 nm remains unchanged, the band around 650 nm shows a strong dependence with temperature. For $T_m$ greater than 200 K, the large band remains unchanged. For $T_m$ less than 150 K, the intensity of the band increases with decreasing temperature and the bands shift towards lower wavelengths. For $T_m$ equal to 77 K, the band is asymmetric with a maximum at 500 nm. It can be deconvoluted with two Gaussian bands centered at 505 and 612 nm. With increasing $T_m$, the intensity of the band at 505 nm decreases very quickly. Its intensity is divided by a factor five from 77 K to 150 K and the band disappears at room temperature. For $T_m$ equal to 77 K, the band is asymmetric with a maximum at 500 nm. It can be deconvoluted with two Gaussian bands centered at 505 and 612 nm. With increasing $T_m$, the intensity of the band at 505 nm decreases very quickly. Its intensity is divided by a factor five from 77 K to 150 K and the band disappears at room temperature. For $T_m$ equal to 77 K, the band is asymmetric with a maximum at 500 nm. It can be deconvoluted with two Gaussian bands centered at 505 and 612 nm. With increasing $T_m$, the intensity of the band at 505 nm decreases very quickly. Its intensity is divided by a factor five from 77 K to 150 K and the band disappears at room temperature.

Luo et al. [15] also studied the temperature dependence of the PL in the SnO$_2$ nanowires and nanobelts from 10 K to room temperature. At temperatures lower than 100 K, the nanowires show an asymmetric, smooth, and broad luminescence band centered at around 470 nm while, at higher temperatures, an asymmetric broad luminescence band centered at about 560 nm is observed. As in our case, the bands can be deconvoluted with bands centered at 470 and 560 nm. The results show that the two different emission peaks shift slightly to lower energy with increasing temperature. The intensity of the emission peak centered at 470 nm decreases rapidly by about four times as the temperature rises from 10 to 100 K, and almost disappears at room temperature. The intensity of the peak centered at 560 nm decreases by about two times from 10 to 100 K and it dominates the luminescence at room temperature. Hence, the temperature has a much larger influence on the intensity of the emission band at 470 nm. As mentioned by Luo et al., these luminescence bands cannot be ascribed to recombination of free excitons. This is generally interpreted as defect states due to Sn or O vacancies introduced during the growth process, which introduce trapping states in the band gap. For the band centered at 470 nm, a strong temperature dependence is observed, which suggests that it is related to a shallow energy level which is not thermally stable for electrons. On the contrary, the smaller temperature dependence of the band centered at 560 nm supposes deeper defect energy level, which is thermally stable.

Nd-doped SnO$_2$ thin films were prepared with Nd concentrations up to 4.3%. The as-deposited sample and those annealed at 300 and 500°C do not show any Nd-related PL signal. For the samples annealed at 700°C, the characteristic PL emissions of Nd$^{3+}$ ions are obtained. The room temperature PL spectra for samples annealed at 700°C in air and having different Nd concentrations are presented in Fig. 7. The peaks at 920, 1100 and 1300 nm are due to transitions from the $^4F_{3/2}$ excited state to the $^4I_{n/2}$ levels with $n$ equal to 13, 11 and 9, respectively. The intensity of these bands increases with the Nd content in the SnO$_2$ matrix up to a Nd concentration equal to 3 %. For higher doping level, the PL intensity decreases. This effect could be attributed to a concentration quenching effect.
characterized by the energy exchange between a pair of Nd ions. This non-radiative process is generally described by a cross-relaxation process in which two neighboring ions are exchanging energy and by the migration of the excitation energy.

The evolution of the PL spectra with the doping level is also correlated to the PL band at around 600 nm, already observed in the undoped sample. For the sample doped with Nd 0.1 %, the intensity of this band is high while the Nd-related peaks are hardly visible. For higher Nd contents, this band disappears. As the excitation wavelength used for the PL measurements is equal to 325 nm, the excitation of the Nd$^{3+}$ ions probably occurs via indirect mechanisms like carrier-mediated processes. An energy-transfer process between defect states giving rise to the luminescence at around 600 nm and the Nd$^{3+}$ ions could be such a process. Indeed the energy value between the ground state and the $^2G_{5/2}$, $^2G_{7/2}$ excited states is equal to 590 nm. Such an energy-transfer process could explain the simultaneous decrease of the wide PL band and the increase of the Nd-related ones.

![Graph](Fig. 8. Room-temperature PL spectra of Tb-doped SnO$_2$ alloys annealed at 700 °C, for different Tb concentrations.)

Tb-doped SnO$_2$ thin films were prepared with Tb concentrations up to 5.5 %. The as-deposited sample and those annealed at 300 and 500°C do not show any Tb-related PL signal. For the samples annealed at 700°C, the characteristic PL emissions of Tb$^{3+}$ ions are obtained, as presented in Fig. 8. The PL spectra show four peaks corresponding to the characteristic $^5D_4 \rightarrow ^7F_j$ ($j = 3–6$) transitions in Tb$^{3+}$ ions. Such bands were already observed by other groups [6,11,16] in Tb-doped SnO$_2$. The concentration effect shows a quenching of the PL intensity for Tb$^{3+}$ concentration above 2 %.

The evolution of the PL properties with the annealing treatments suggests that the SnO$_2$ rutile structure is needed to optically activate the RE$^{3+}$ ions. It is known that the electric dipole transition between intra 4$f$ states are forbidden for isolated rare earth ions. The crystal field can however contribute to relax this selection rule by mixing states having different parities [17]. The optical activity of the RE ions is then strongly dependent on the magnitude of the crystal field which in turns depends on the symmetry of the occupied site and on the RE-ligands bonds. Ionic RE-ligand bonds are assumed to strength the coupling to the lattice and then favour the luminescence. Oxygen atoms are then good candidates to increase the optical activation of RE$^{3+}$ ions, which could explain the strong PL for the sample annealed above 700 °C.

4. Conclusion

In conclusion, we have fabricated Nd-doped and Tb-doped SnO$_2$ layers by evaporation of SnO$_2$ powder combined with Nd or Tb effusion. The RE-doped SnO$_2$ films are found to be photoluminescent. The optical activation of the RE$^{3+}$ ions is obtained, when the sample has the tetragonal structure of the SnO$_2$ rutile phase, which is obtained after an annealing treatment at 700 °C in air. The SnO$_2$ host matrix allowed to introduce Nd$^{3+}$ and Tb$^{3+}$ ions with a concentration as large as 3 and 2 %, respectively, without any concentration quenching.
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References