Optical excitation of charge carriers from intra-bandgap states in Ce-doped SnO_2 thin films

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Abstract. Optical excitation of Ce^{3+}-doped SnO_2 thin films, obtained by the sol-gel-dip-coating technique, is carried out and the effects on electrical transport are evaluated. Samples are doped with 0.1at% of Ce, just above the saturation limit. The excitation is done with an intensity-controlled halogen-tungsten lamp through an interference filter, yielding an excitation wavelength of 513nm, 9 nm wide (width at half intensity peak). Irradiation at low temperature (25K) yields a conductivity increase much lower than above bandgap light. Such a behavior assures the ionization of intra-bandgap defect levels, since the filter does not allow excitation of electron-hole pairs, what would happen only in the UV range (below about 350nm). The decay of intra-bandgap excited levels in the range 250-320 K is recorded, leading to a temperature dependent behavior related to a thermally excited capture cross section for the dominating defect level.

Keywords: Thin films, tin dioxide, cerium, electroluminescent devices.
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INTRODUCTION

Optoelectronic integrated devices require materials with low optical loss, and doped with optically active elements such as rare earths (RE), which present radiative transitions in a large wavelength range. Combination of RE core transition with wide bandgap semiconductors induces high emission efficiency. SnO_2 is a wide bandgap semiconductor (3.6eV) and has been used as matrix for phosphorescent materials [1,2]. Ce^{3+} ion presents $4f^1$ electronic configuration at the ground state and $5d^1$ at excited state. Optical transitions between these states are allowed electric dipole transitions. Level 5d presents strongly lattice interaction and the first dipole transition suffers a spectroscopic redshift when incorporated into a crystal, being shifted towards lower energy compared to the free ion [3]. Optical excitation of different types of glasses yields emission in the range 300 to 450 nm, depending on the matrix [4]. Broad blue-green emission has been recorded around 489nm, being attributed to the transition from 5d excited level (^2D) to 4f ground state of Ce^{3+} [5]. The ground state of the Ce^{3+} ion is a doublet ($^2F_{5/2}$ and $^2F_{7/2}$) and then, the emission from the 5d excited state is expected to show two peaks, which usually does not happen due to the lack of specific symmetry or long-range periodicity in the matrix [4]. The knowledge of optically excited electrical characteristics in Ce-doped SnO_2 is fundamental for design and operation of electroluminescent devices. Recently a blue electroluminescence emission (440nm) in Ce^{3+} -doped SiO_2 has been reported, where the emission has its efficiency increased by codoping with Gd^{3+}, caused by a energy transfer process [6]. In order to investigate electroluminescent characteristics of Ce^{3+}-doped SnO_2 thin films, the optical ionization of Ce-related defects and the analysis of charge trapping back may become a very important tool, since it combines optical and electrical properties of Ce-doped SnO_2 thin films. Ce^{3+} is incorporated into SnO_2 lattice substitutional in Sn^{4+} sites and exhibits an acceptor like behavior in tin dioxide [7], leading to a high degree of electrical charge compensation, and high resistivity films. Recombination of electron-hole pairs with desorbed oxygen species leads to persistent photoconductivity (PPC) effect [8] in undoped SnO_2 sol-gel thin films at low temperature [7], and to an exponential-like decay for RE-doped SnO_2. The decay of photo-excited conductivity can be applied in order to understand the

electron trapping phenomena [9]. The experiment may be summarized as follows: a monochromatic excitation may ionize intra-bandgap defects and electron-hole pairs, depending on the energy of the excitation irradiation. After removing the illumination, the time-temperature dependence of charge carrier trapping by defects is measured and the thermally activated capture cross section of the dominating level is evaluated. Recently, the decay of excited conductivity of Er-doped SnO_2 have been recorded and the carrier trapping by Er-related defects have been modeled [7,9], where the excitation is obtained with the fourth harmonic of a Nd:YAG laser (266nm), which leads to ionization of intra-bandgap defect centers along with electron-hole pairs.

This communication deals with optical excitation of Ce^{3+}-doped SnO_2 thin films excited by below bandgap light. Excitation is done with a wavelength of 513nm. The decay of intra-bandgap excited levels in the range 250-320 K is recorded, leading to a temperature dependent behavior and a thermally excited capture cross section for the dominating level, which is presently being modeled.

EXPERIMENTAL

Colloidal suspension were produced by the sol-gel process, from a solution of $SnCl_4.5H_2O$ and $Ce(NO_3)_3.6H_2O$. Initially, the 0.5 mol.L^{-1} $SnCl_4.5H_2O$ aqueous solution is prepared, followed by addition of an appropriate amount of $Ce(NO_3)_3.6H_2O$ in order to obtain the desired doping of Ce^{+3}. Concentrated NH_4OH is added to the solution under stirring with a magnetic bar, until no more precipitation takes place (pH 11). This procedure provides a viscous and whitish solution and the resulting suspension is submitted to dialysis against distilled water for about 10 days for elimination of Cl^- and NH_4^+ ions. Thin films are deposited by dip-coating technique on borosilicate glass substrates with a withdrawal rate of 10cm/min. Layers are deposited at room temperature, gelling in air for 20 min and fired at 400°C for 10 min in a furnace at room pressure. When the total of 10 layers is reached, samples are submitted to thermal annealing at 550°C for 1 hour in the same furnace. Resulting thickness of films obtained by this procedure is about 360nm, as evaluated from scanning electron microscopy of cross section.

To accomplish electrical measurements, tin electrodes have been evaporated through resistive evaporation technique, with 10^{-5} torr of pressure in an EDWARDS Auto 306 evaporation system, using a molybdenum crucible. Sn electrodes were submitted to thermal annealing at 180°C for 30 minutes. Current as function of temperature measurements were carried out in a closed helium circuit cryostat of APD Cryogenics, coupled with a Lake Shore temperature controller with 0.05 degree of precision. For the excitation and decay of photo-induced conductivity measurements, samples were irradiated with an intensity-controlled halogen-tungsten lamp (Oriel) through an interference filter, yielding an excitation wavelength of 513nm, 9 nm wide (width at half intensity peak). For the shown data of conductivity decay of Er^{3+}doped SnO_2 thin film, samples were irradiated with the fourth harmonic (266nm) of an Nd:YAG pulsed laser, with 10 Hz of pulse frequency, by 10 min, keeping constant temperature. More details on Er-doped samples and conductivity decay measurements have been published elsewhere [9]. Data are shown here only for comparison.

RESULTS –DISCUSSION

Figure 1 shows results of resistivity as function of temperature for a SnO_2:1.0at%Ce^{3+} thin film in the dark and under irradiation with light from a halogen-tungsten lamp through several types of band pass filters. The inset of figure 1 is the same sort or result, for a SnO_2:0.1atCe^{3+} thin film irradiated with light from the same source but passing through the described interference filter. The most doped sample presents a very high resistivity even at room temperature (about 10^5ohm.cm) and them, the variation with temperature, even in the dark is not very large. By the other hand, in the inset of figure 1, a variation of three orders of magnitude can be observed from room temperature to 25 K. Irradiation at low temperature (25K) yields a conductivity increase, which is higher depending on the intensity of irradiating light (measured by the current through the lamp filament of the W irradiation source). Such a behavior assures the ionization of only intra-bandgap defect levels, since the filter does not allow excitation of electron-hole pairs, what would happen only in the UV range (below about 350nm). This sort of measurement is carried out to find out the most suitable system to provide intensity enough to excite intrabandgap states and to avoid electron–hole pairs. It is easily verified in figure 1 that combination of W source with 350nm band pass filter practically destroys the sample resistivity. On the other hand, illumination through the 550nm band pass filter increases only slightly the current, and only in some temperature range, independent of the light intensity.

Concerning the illumination through the interference filter, the conductivity clearly increases with the intensity and due to its wavelength, it assures no electron-hole generation.

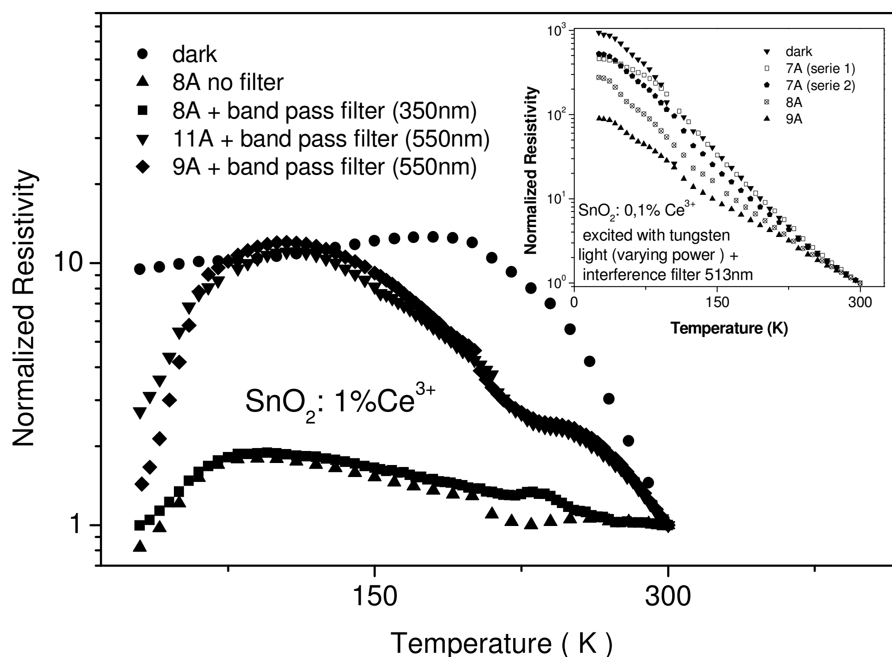

FIGURE 1. Resistivity normalized by its room temperature value for SnO_2:1.0at%Ce^{3+} excited with a tungsten lamp plus band pass filters. Inset: the same type of result for SnO_2:0.1at%Ce^{3+} with an interference filter (513nm) with several electrical currents through the lamp filament.

Figure 2 shows the time dependent conductivity excitation with tungsten light passing through the interference filter (around 2.40eV). For the lower temperature the conductivity follows a exponential-like increase whereas for room temperature and above it seems that the exponential-like excitation behavior at the beginning of the curve is modified for a higher intensity increase from about 100 s. This behavior is quite different when compared to the Nd:YAG excitation, which provides electron-hole generation (above SnO_2 bandgap energy), and yields a exponential-like behavior, tending to saturation. The inset in figure 2 is a sketched diagram showing the relative optical excitation of electron-hole and Ce^{+3} levels, inside the bandgap. The behavior of the time-dependent excitation process raises the possibility that the electron release from intrabandgap states can be a two step excitation process, for distinct dominating time ranges.

Figure 3 shows the exponential-like conductivity decay of the intra-bandgap trapping. The inferior inset shows the exponential fit of the decay at 250K, although the noise is rather significant. The superior inset of figure 3 brings an conductivity decay for Er-doped SnO_2 with 0.1at%Er, excited with the fourth harmonic of a Nd:YAG laser (4.65eV). It is easily seen in figure 3 that the decay is much more evident for the excitation with the laser. The conductivity decay from SnO_2:0.1at%Ce thin film presents much less intensity. The excitation of the intrabandgap states with the lamp plus interference filter is not as easy to measure as the decay generated by the laser, then the noise becomes much more difficult to avoid due to the lower signal. Although this electrical noise is not negligible, it can be figured from figure 3 that the higher the temperature the faster the decay. This result is as expected from a defect level presenting a thermally activated capture section. Then, more precise measurements, varying Ce^{3+} concentration, decay time and temperature, and using a hardware improvement in order to prevent noise, shall bring a complete measurement data set.

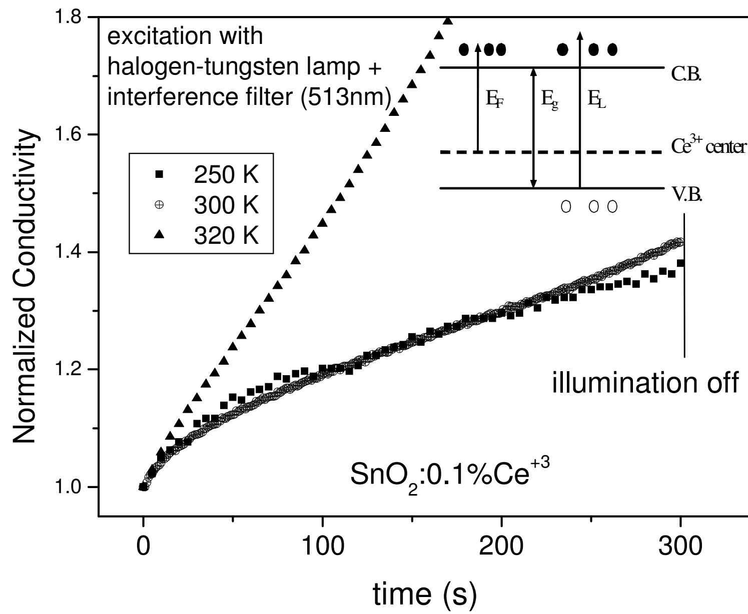

Figure 2 SnO_2:0.1at%Ce^{3+} excited with a W light plus interference filter as function of exposure time, for some distinct temperatures. Inset – excitation simplified diagram. E_g – SnO_2 bandgap (3.6eV), E_L – 4th harmonic Nd:YAG laser (4.65eV), E_F – W source plus interference filter (2.41 eV).

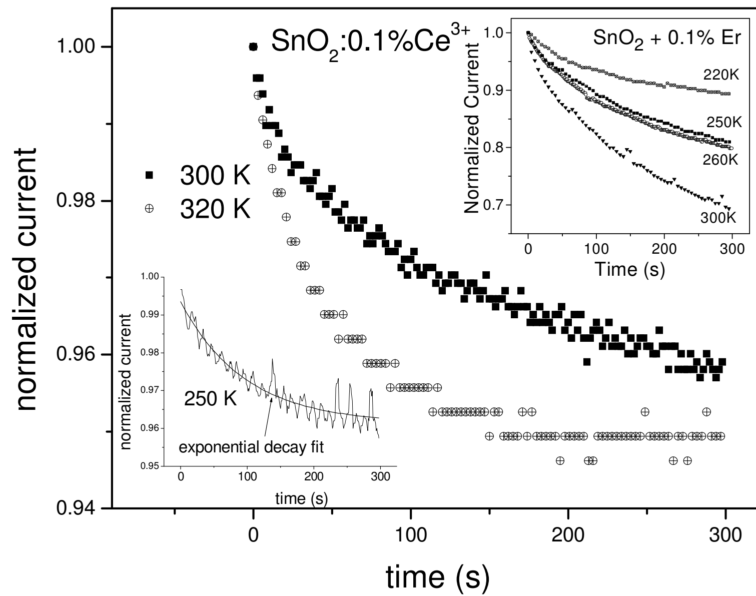

FIGURE 3. Decay of excited conductivity in SnO_2:0.1at%Ce^{3+} for two temperatures. Inferior inset: the same measurement for 250K along with an exponential like fit. These decays are excited with W lamp plus interference filter. Superior inset: conductivity decay for SnO_2:0.1at%Er^{3+} excited with the fourth harmonic of a Nd:YAG laser (266nm)

The observed decay of conductivity as function of time means that the resistance of the film increases with time. The decay of photo-induced electrons (n) from the conduction band to the trapping defect is given by [8]:

$$\frac{dn}{dt} = -C_n.N_{Def}^{+} \tag{1}$$

where C_n= $V_{th}.\gamma_n$.n, V_{th} is the thermal velocity of free electrons, $\gamma_n=\gamma_\infty.\exp(-E_{cap}/kT)$ is the capture cross section, E_{cap} is the potential barrier for electron trapping and γ_∞ is the constant capture cross section (infinite temperature). N_{Def}^{+} is the number of ionized defects, which is Supposed as singly ionized, then: $N_{Def}^{o} \rightarrow e^{-} + N_{Def}^{+}$ and then $N_{Def}^{+} = n$, where it is considered that decay time is long enough to neglect electron-hole recombination.

From equation (1), and with the help of a straightforward derivation [9], it can be shown that the variation of sample resistivity with time and temperature can be used to obtain important parameters related to electronic mobility. It can be shown that [9]:

$$\frac{dR}{dt} = slope = K_f.T.\exp\left[-\frac{E_{cap}-\phi}{kT}\right] \tag{2}$$

where E_{cap} is the potential barrier for carrier capture and ϕ is the potential barrier at grain boundary. K_f is a constant [9]. A plot of ln(*slope*/T) as function of 1/T yields the quantity (E_{cap}-ϕ) directly from the curve inclination. The complete measurement set presented in the inset of figure 3 for SnO_2:0.1at%Er and considering ϕ as a constant value (30meV) [10], provides the evaluation of the capture barrier, yielding a value of 108eV.

This model, for trapping by intrabandgap states in under progress and will take into account the capture barrier and the ionization energy of the two distinct levels as possibly observed by excitation from room temperature. Our model for the decay of conductivity for above bandgap excitation in SnO_2:Er has lead to three distinct levels [11]: oxygen vacancy, which is dominating for undoped SnO_2 thin films, Er^{3+} located at grain boundary, domination for SnO_2 thin films with Er concentration above the saturation limit (about 0.1%atEr [12]) and substitutional to Sn^{4+} sites, which is the governing trapping level below the saturation limit

CONCLUSION

The decay of the photo-induced conductivity is rather different depending on the wavelength of the excitation light. Above bandgap monochromatic light, coming from the 4th harmonic of a Nd:YAG laser induces electron hole generation along with excitation from intrabandgap states. On the other hand, the combination of a W source with a interference filter yields a lower conductivity signal and the decay is more subject to electrical noise. A model for the decay of the excited conductivity has been proposed and its application for Ce^{3+}-doped SnO_2 samples shall lead the capture barrier by the intra-bandgap Ce^{3+} centers. In this communication we present for the first time the signal recorded for this material and the modeling is under progress.

This paper is a contribution in the direction of the complete knowledge of electro-optical characteristics of Ce-doped SnO_2 thin films. Along with emission characteristics in the blue-green region, this understanding is fundamental towards the building of electroluminescent devices, operating on this wavelength range.

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