



Optical emission and electron capture of rare-earth trivalent ions located at distinct sites in SnO₂ thin films

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Abstract

We present photoluminescence and decay of photo excited conductivity data for sol-gel SnO₂ thin films doped with rare earth ions Eu³⁺ and Er³⁺, a material with nanoscopic crystallites. Photoluminescence spectra are obtained under excitation with several monochromatic light sources, such as Kr⁺ and Ar⁺ lasers, Xe lamp plus a selective monochromator with UV grating, and the fourth harmonic of a Nd:YAG laser (4.65eV), which assures band-to-band transition and energy transfer to the ion located at matrix sites, substitutional to Sn⁴⁺. The luminescence structure is rather different depending on the location of the rare-earth doping, at lattice symmetric sites or segregated at grain boundary layer, where it is placed in asymmetric sites. The decay of photo-excited conductivity also shows different trapping rate depending on the rare-earth concentration. For Er-doped films, above the saturation limit, the evaluated capture energy is higher than for films with concentration below the limit, in good agreement with the different behaviour obtained from luminescence data. For Eu-doped films, the difference between capture energy and grain boundary barrier is not so evident, even though the luminescence spectra are rather distinct.

Key words: rare-earth, tin dioxide, sol-gel, erbium, europium

1. Introduction

Tin dioxide (SnO_2) is a wide bandgap semiconductor (about 3.6eV), [1,2] which presents high transparency in the visible (above 90%) and high reflectivity in the infrared [3]. In the undoped form, this compound exhibits n-type conductivity, due to oxygen vacancies and interstitial tin atoms, generated during sample processing. The wide bandgap makes SnO_2 an attractive matrix for electrically activated emission [4], since wide bandgap semiconductors have higher excitonic ionization energy. Besides, the wide gap decreases the luminescence quenching effects [5]. Research on electroluminescent displays involves mainly investigation of electro-optical behavior of luminescent materials. One of the most promising display technologies is the thin film electroluminescence (TFEL). Among the TFEL devices, luminescent properties are related to intra 4f rare-earth transition [6], mainly the ions Eu^{3+} and Er^{3+} , because their transitions take place on a wide energy range, with emissions from the visible to the infrared, allowing application in several optical communication devices.

We have investigated optical and optically induced electrical properties of Eu and Er doped SnO_2 thin films and xerogels (powder), through measurements of photoluminescence and decay of photo-induced conductivity. The acceptor nature of ions Er^{3+} and Eu^{3+} [7,8] creates a high charge compensation degree in the material, leading to a high resistivity compensated semiconductor. When produced by the sol-gel process, SnO_2 thin film presents nanoscopic crystallites (about 5-10nm). This nanostructured material exhibits a high concentration of grain interfaces by unit area, which favors the impact ionization of luminescent centers, because hot carriers are promoted by the interface active layer/dielectric in a TFEL device layout [9].

The electrical properties are strongly influenced by grain boundary scattering. Electrical and optical properties of SnO_2 thin films are related to location of the doping impurity in the matrix. The luminescent fine structure as well as the lifetime of excited carriers are determined by the substitutional position of the trivalent rare-earth (RE^{3+}) at Sn^{4+} sites or segregated at grain boundary.

In this work, we have measured the luminescence spectra by excitation with several distinct light sources, such as Kr^+ , Ar^+ and Nd:YAG lasers. Emission from these rare-earth ions also leads to different shapes of luminescence spectra whether the dominant luminescent center presents high symmetry, at lattice sites, or is located at asymmetric sites, segregated at boundary layer. Thin films are also excited with the fourth harmonic of an Nd:YAG laser (4.65eV) at low temperature, yielding conductivity decay when the illumination is removed, which is related with capture by rare-earth related defects. Based on a model proposed elsewhere [10], where trapping defects present thermally activated cross section, E_{cap} (capture energy) is evaluated, leading to distinct trapping centers: substitutional at Sn^{4+} lattice sites and located at grain boundary interface. The thin film matrix presents a very useful shape for technological

application, since it allows optical integration and the application of electric fields to operate electroluminescent devices.

2. Experimental

Colloidal suspensions of SnO_2 undoped and doped with Er^{3+} or Eu^{3+} have been prepared through the sol-gel route. Firstly, it has been prepared an aqueous solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.5 M). Doping with Eu has been provided by dissolution of Eu_2O_3 in HCl, being the desired amount added to the starting solution. In the case of Er doping, the reagent used was $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$. Under stirring with a magnetic bar, NH_4OH was then added until the pH reaches 11, leading to hydrolysis and condensation reactions. The remaining precipitated was submitted to dialysis against distilled water for about 10 days, in order to eliminate Cl^- and NH_4^+ ions. This procedure leads to a stable suspensions (sol) of $\text{SnO}_2\text{:Eu}$ and $\text{SnO}_2\text{:Er}$. Xerogels (powders) were obtained by drying the suspension at room conditions and treated at 1000°C during 6 hours. For photoluminescence (PL) measurements at low temperature, the xerogel (powder) was treated at 1000°C during 6 hours and compressed down with $5 \times 10^3 \text{ kgf/cm}^2$ of load to the shape of a pellet. Sample cooling was done in a He closed-cycle cryostat from Janis.

For luminescence data presented here a few experimental setups were used: (1) for low temperature measurements, an Ar^+ laser from Spectra Physics model 2017 for sample excitation and signal recorded by a germanium detector from Edinburgh Instruments. (2) a xenon lamp of 450W, a fluorimeter SPEX F212I and a germanium detector North Coast Scient. Corporation model EO-8171. (3) excitation with a Kr^+ laser, tuned on an ultraviolet multi-line mode (3.67eV, 3.53eV and 3.47eV), (4) excitation with a Kr^+ laser, tuned on 2.56eV. A photomultiplier tube (PMT) R446 from Hamamatsu was used for signal measuring and recording in the methods 3 and 4. (5) Sample excitation with the fourth harmonic of a Nd:YAG laser, 4.65eV. The signal was detected by a CCD detector coupled with a Jobin Yvon monochromator, model T64000.

For the decay of photo-excited conductivity, it was used the fourth harmonic of a pulsed Nd:YAG laser (4.65eV), with 15Hz of frequency, and a Keithley 6517A for recording electrical characteristics.

3. Results and discussion

Figure 1 (a) shows temperature dependence of photoluminescence (PL) spectra measured at temperatures 50 K and 280 K for a 2at% Er doped SnO_2 xerogel sample. Sample was excited with an Ar^+ laser, operating with 2.53eV of excitation energy (method 1). The Er^{3+} transition

$^4I_{13/2} \rightarrow ^4I_{15/2}$ around 0.8eV is clearly evidenced by the presence of several peaks. The excitation energy (2.53eV) corresponds to the transition from ground state to $^4F_{7/2}$. The inset of Figure 1(a) shows PL spectra for tin dioxide xerogel codoped with 2at% of Er and Yb, excited by a Xenon lamp plus a monochromator (method 2). It can be noticed in figure 1 that temperature decrease leads to PL intensity increase, since the cooling down decreases the lattice vibration of SnO_2 , and then phonon assisted nonradiative processes, which enhance light emission from Er^{3+} core transition. It allows the observation of details at low temperature spectra not observed at higher temperatures. In the measurement carried out at 50 K, it is clearly seen the presence of others peaks not observed at 280 K. This vanishing is probably related to lattice vibration. All the observed peaks are related to the decay of excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$. The presence of several peaks can be attributed to the splitting of $^4I_{13/2}$ and $^4I_{15/2}$ levels due to the matrix crystalline field [11]. The Er^{3+} $^4I_{13/2}$ manifold has upper states of the excited degenerate $^4I_{13/2}$ level populated due to local laser heating [11], as evidenced by the fact that such a line splitting does not takes place when the sample is irradiated with monochromatic light coming from a xenon lamp (inset of fig. 1(a)). In the inset of figure 1(a), the two different excitation wavelengths were used: 3.77eV and 2.35eV. The codoping with Yb^{3+} allows verifying the energy transfer process, by exciting with 1.26eV, corresponding to transition $^2F_{7/2} \rightarrow ^2F_{5/2}$ of Yb^{3+} and an energy transfer to transition $^2F_{7/2} \rightarrow ^4I_{11/2}$ of Er^{3+} . However the verification of this energy transfer process is not the scope of this paper, and has been done elsewhere [12]. Investigation of PL spectra of $\text{SnO}_2\text{:Er,Yb}$ xerogels with doping concentration of 0.1at% has yield information on Er localization in the matrix [12]. When the excitation is done with the energy coincident with the SnO_2 bandgap transition, the shape of the observed spectra is typical of substitutional Er emission. On the other hand, under direct excitation of Er^{3+} ions, a typical emission of rare center in a vitreous matrix is observed [13]. Two families of Er sites were found in SnO_2 : substitutional to Sn^{4+} and segregated at boundary layer. The second family is related to the solubility limit of rare-earth (RE) ions in tin dioxide, which is about 0.05at%, and the doping excess become located at boundary layer [14]. For the high doping concentration (2 to 4%) of the samples reported here, it is expected very many Er complexes segregated at boundary layer. The inset of figure 1(a) shows the emission of Er^{3+} at room temperature, excited directly. The spectra observed by excitation with 2.35eV, which presents a broadened PL shape, is similar to a luminescent center of a vitreous matrix (amorphous) [13], with no well defined components as the sample excited at 3.77eV (peaking at 1512, 1525 and 1543nm). However, it is clearly observed the presence of the component at 1543nm in the upper spectra, suggesting a convolution of spectra of two families of Er in SnO_2 . Besides, this spectra is similar to the observed by excitation with 1.26eV. Considering that the codoping with Yb^{3+} is efficient only for Er^{3+} ions located at grain boundary [12], we may assure that this energy excites only grain boundary located ions. On the other hand, the rare-earth ions located at Sn^{4+} sites are not

substantially excited by this indirect procedure. Some papers [12,15,16] state that substitutional sites located Er^{3+} ions are excited via band-to-band excitation of SnO_2 and the spectra is as shown in the inset of figure 1(a) by 3.77eV excitation.

Figure 1(b) shows the green emission from an Er doped (4%) SnO_2 thin film excited with a Kr^+ laser, tuned on the ultraviolet multi-line mode (method 3), and the emission from a SnO_2 :2%Er pellet, excited with a Kr^+ laser, tuned on 2.56eV (method 4). The energy range in both curves of figure 1(b) are in good agreement and assures that the observed wide emission, with a peak about 2.33eV, includes the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ radiative transition of Er^{3+} ion. This broad shape is probably related to random neighborhood of Er^{3+} at the SnO_2 lattice, which could be surrounded by varying number of oxygen vacancy, interstitial tin atoms and grain boundary, since we are dealing with nanoscopic grains, in the range 5-10nm. Besides, the excess of Er is located at grain boundary, as discussed for figure 1(a), which are low symmetry sites and could contribute to the broad band. Luminescence from the matrix of SnO_2 itself has been recently reported [17], with very similar shape to the curves of figure 1(b). However it is shifted to UV-violet, presenting a peak about 3.1eV, which was attributed to oxygen vacancies. The observed broad band green emission centered about 2.33eV is the transition from the excited state $^2\text{H}_{11/2}$ to the $^4\text{I}_{15/2}$ ground state. In the spectrum of figure 1(b), film is excited with the multilines UV from a Kr^+ laser (most intense line at 3.53eV). Figure 1(b) also shows photoluminescence (PL) emission from a pellet (powder compressed) of SnO_2 :2%Er, with excitation with 2.56eV, which is coincident with $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$ transition. Although the laser line at 2.56eV is not enough to excite the green transition in the SnO_2 :4at%Er film, it is accountable for the excitation of observed transition in SnO_2 :2%Er pellet. It means that to obtain efficiently the transition, the number of exciting centers in the beam light path becomes very relevant. This path is rather long for the pellets but much shorter for the film. However our results in the visible range make sure that luminescence is possible also for the film, which justifies investigation of film emission in the infrared. Crystallite nanoscopic dimensions could play a relevant role in the emission spectra, due to the possibility of quantum confinement effects [18,19].

Figure 2 shows photoluminescence of excitation (PLE) spectra of Er – doped SnO_2 thin films with several concentrations of doping. In this procedure, light from the 450 W xenon lamp is selectively monochromated into the sample and the photoluminescence coming out the sample due to this excitation is received by the sensor, passing through another monochromator fixed at 1525nm. In these spectra, it is clearly verified that excitation with light of the SnO_2 bandgap (about 3.5eV) is responsible for a high emission of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition. The intensities cannot be compared because the monochromator slit opening was not maintained constant for all the spectra. However, independent on the concentration, there is some emission coming from the band-to-band energy transfer, which means that for a very low concentration as well as for way above the saturation limit, substitutional Er^{3+} ions always present some emission. Besides

it is possible to observe that the excitation $^4I_{15/2} \rightarrow ^2H_{11/2}$ also gives rise to the infrared emission, but with less intensity. A slight shift in the peak position is seen, what also could be attributed to quantum confinement effects in the nanoscopic sized crystallites.

Figure 3 shows PL spectra obtained under excitation with 4.65eV (266nm) laser line (method 5) for Eu-doped SnO_2 xerogels with 1.0 and 0.5 at% Eu concentrations. The inset of Figure 3 shows PL spectra of 0.5%Er doped SnO_2 xerogel, under excitation with 4.65eV and 2.53eV (488nm). It is important to point out the nature of the transitions $^5D_0 \rightarrow ^7F_2$ (2.02eV) and $^5D_0 \rightarrow ^7F_1$ (2.10eV), labeled in figure 3. The latter one is a magnetic dipole transition and its intensity is not affected by structural changes of the nearest neighborhood, whereas the transition $^5D_0 \rightarrow ^7F_2$ is ruled by electric dipoles, being hypersensitive to the local crystalline field [20]. The ratio between the areas of these emission lines, i.e., $^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ is called asymmetric ratio. An increase of asymmetry ratio from 0.01 to 5.2 is evaluated for samples with 0.5 to 1at% Eu, respectively, which means that for increasing Eu^{3+} concentration, energy transfer is more efficient to ions located far from the symmetry center, for instance, ions located close to the particles surface. For $\text{SnO}_2:0.5\%\text{Eu}^{3+}$ samples the PL line shape suggests an asymmetric ratio very close to zero, indicating that Eu^{3+} is actually located at lattice sites, substitutional to Sn^{4+} in the C_{2h} sites of rutile structure of SnO_2 matrix. The xerogel $\text{SnO}_2:1\text{at}\%\text{Eu}$ presents PL spectra with the electric dipole $^5D_0 \rightarrow ^7F_2$ transition as dominant, suggesting that the Eu^{3+} ion is located close to the particles surface, with low symmetry. The excess of doping must cause the energy transfer to the Eu^{3+} sites belonging to the SnO_2 lattice to be less effective, when compared to luminescence from other centers with lesser symmetry. This behavior may be also related with decrease of particle size with increasing of Eu concentration. X-ray diffractograms for undoped and Eu-doped xerogels evidences that doping decreases the particle size. In other words, there is a decrease of the particle size as the Eu concentration increases. Excitation with 4.65eV leads to a very well defined PL spectra, with peaks centered at 2.11, 2.09 and 2.07eV, corresponding to the three components of $^5D_0 \rightarrow ^7F_1$, as clearly observed in figure 3. In this case, the observed emission at 2.02eV ($^5D_0 \rightarrow ^7F_2$) presents low intensity. Then the asymmetric ratio is very close to zero, indicating that Eu^{3+} is actually located at lattice sites, substitutional to Sn^{4+} in the SnO_2 matrix [13], as already discussed. On the other hand, directly excitation of Eu^{3+} ion with 2.53eV leads to an increase of the asymmetric ratio, as can be seen in the inset of figure 3, for $\text{SnO}_2:0.5\text{at}\%\text{Eu}$. The solubility limit of Eu in SnO_2 is about 0.05 to 0.06at% [14]. Then the excess of Eu segregates to particle surface, giving rise to a non-homogeneous impurity distribution. The observed broadening in the PL emission may be related to Eu^{3+} ions segregated at particle surface with random distribution of first neighbors. Then, similar to the analyses carried out for Er^{3+} doping we may conclude that the emission of Eu^{3+} substitutional in the SnO_2 lattice is more evident under excitation band-to-band

of SnO₂, suggesting a high energy transfer from the matrix due bandgap energy excitation. It is also possible to verify that the emission from Eu³⁺ ions located close to particles surface is more clearly observed by direct excitation of ⁷F₂→⁵D₂ transition with the 2.53eV laser line.

Figure 4(a) and 4(b) bring results of decay of photo-excited conductivity at several temperatures, for thin films of SnO₂ doped with 0.1at% and 1at% of Eu³⁺, respectively. In this measurement, films were irradiated with the fourth harmonic of a Nd:YAG laser (4.65eV), the same used in the method 5 of PL excitation, promoting electron-hole pair excitation, increasing the number of charge carriers in the conduction band and thus, the material conductivity. After 10 min of light irradiation, time enough to the excitation lead to a carrier saturation, laser illumination was removed and the decay of current was measured as function of time. Fig. 4(c) shows resistivity as function of temperature for SnO₂ thin films doped with 0.1%Er and 0.1%Eu, in the dark and a long time after being submitted to laser irradiation, corresponding to the measured decay presented in figures 4(a) and 4(b). As can be seen in figure 4(c), the Eu³⁺ sample present a higher resistivity when compared to Er³⁺ doped films, which is probably related to the larger size of Eu³⁺ [21]. Besides the figure 4(c) also allows verifying the long lasting persistent photoconductivity phenomena in rare-earth doped SnO₂ films [22]. As the Er-doped sample remains a longer time under low pressure, its resistivity becomes higher than the Eu-doped film, due to slow oxygen adsorption. Figure 4 allows verifying that there is a concentration dependent decay of photoexcited current as well as a temperature dependency. Increasing the temperature and Eu concentration, the capture rate also increases, leading to a faster decay. According with the electron capture model presented previously [8,10], by the inclination of this curve, the quantity ($E_{\text{cap}} - \phi$) is obtained, where E_{cap} is the trapping energy barrier, related to a relaxation process and ϕ is the grain boundary potential barrier. In this model, we consider the electron scattering at grain boundary as the dominant mechanism for the conductivity [8], which is a reasonable assumption due to the nanoscopic dimensions of grains. Average values where obtained for the films, leading to 113meV and 116meV, for 0.1% and 1at% doped films, respectively.

Recently, we have found the existence of different centers in thin films of SnO₂:Er, through measurements of decay of photoexcited conductivity [8,10]. The electron trapping energy by defects are related to oxygen vacancies as well as rare earth centers. Both types of defects are active in the capture process, but they present distinct capture cross section and trapping times. There is a strong indication that the trapping by Er³⁺ centers is dominant by short times, and for longer times the capture by oxygen vacancies becomes a competitive process. A larger variation in the quantity ($E_{\text{cap}} - \phi$) was found for Er³⁺-doped SnO₂ thin films [8,10], when the doping concentration is greatly varied, being found energies of 78, 70 and 118meV for 0.05, 0.1 and 4at% de Er³⁺, respectively. Increasing the concentration from 0.05at% to 0.1at%, we

observed a lower capture barrier, which is consistent with a faster decay detected in these measurements. By the other hand, when the Er^{3+} concentration increases to a high value (4at%), the value of $(E_{\text{cap}} - \phi)$ increases, which has been interpreted as due to distinct location of Er^{3+} -related traps, in the lattice, substitutional to Sn^{4+} and in the particles surface. The increase in the value of $(E_{\text{cap}} - \phi)$ may be related to the presence of oxygen vacancies at grain boundary, which is reinforced by EXAFS measurements at K edge of Sb^{+5} in Sb-doped SnO_2 thin films [23], where it was verified that an increase in the doping concentration decreases the barrier height between grains. Then, if ϕ decreases, $(E_{\text{cap}} - \phi)$ may increase. Comparing $(E_{\text{cap}} - \phi)$ for SnO_2 : 0.1at% Er^{3+} and SnO_2 : 0.1at% Eu^{3+} , assuming that the intergrain potential barrier (ϕ) has the same height for both samples, the capture barrier (E_{cap}) is higher for Eu doping, which is consistent with a higher disorder obtained by the calculation of structural refinement of these samples. EXAFS and XANES measurements are presently being prepared to be carried out for Er and Eu doped SnO_2 thin films and xerogels, and must be conclusive on the ion location and oxidation states, depending on the rare-earth concentration.

4. Conclusions

Temperature dependent excitation of 2at%Er in SnO_2 with 2.53eV promoted the excitation of ions Er^{3+} to its $^4\text{F}_{7/2}$ level and the probable decay to nonradiative level $^4\text{I}_{13/2}$, with subsequent emission to the ground state $^4\text{I}_{15/2}$, which means emission in the technologically interesting range 0.8eV. Broad visible emission from Er-doped thin film has been observed with peak about 2.33eV (green). It corresponds to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ radiative transition of Er^{3+} ion. The broad band profile may be related to the random distribution of oxygen vacancy and interstitial tin atoms in the neighborhood of the Er^{3+} lattice sites, substitutional to Sn^{4+} or segregated at grain boundary, which are low symmetry sites.

Eu-doped SnO_2 xerogels emission using 4.65eV and 2.53eV laser lines as excitation sources, allows distinguishing two Eu^{3+} families in SnO_2 : one located in the lattice sites, substitutional to Sn^{4+} , and another one, where rare-earth impurity gets preferentially at particles surface due to segregation caused by excess of doping. Excitation with 4.65eV promotes matrix band-to-band excitation and an efficient energy transfer to Eu^{3+} substitutional to Sn^{4+} . Above the saturation limit, energy transfer is no longer efficient to Eu^{3+} at lattice sites and the energy transfer to ions located close to the particles surface, with lower symmetry, becomes operative.

The difference of capture barrier by the defects and intergrain potential barrier can be evaluated by a trapping model of photo-induced carriers as published elsewhere [8]. Its application for the thin films studied here, leads to higher capture energy for samples doped

with Eu^{3+} compared to Er^{3+} , which may be a indication that the lattice relaxation is higher for the Eu-centers, even though the lattice relaxation mechanism in these films is still unknown.

The results shown in this paper are very promising under a technological point-of-view, since it reveals the possibility of controlling the emission from Er and Eu-doped SnO_2 concerning luminescence spectra structure through rare earth concentration and excitation procedure. Besides, we report emission from thin film, which is a very useful format for this material, since allows the integration in optical systems and makes the electroluminescence phenomena in this material a reality in a very short time.

Acknowledgments

The authors wish to express their gratitude to Drs. A. Tabata, M. R Fernandes, M. S. Li and S. J L Ribeiro for their help with PL measurements in many ways. Authors also thank Brazilian financial agencies: CAPES, CNPq and FAPESP. Luis V A Scalvi thanks FAPESP for participation at ICL 2008.

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Figure Captions

Fig.1 – (a) Photoluminescence (PL) spectra for 2at% Er doped SnO_2 xerogel at 50 K and 280K. Sample was excited with an Ar^+ laser, operating with 2.53eV of excitation energy. Inset - PL of $\text{SnO}_2\text{:Er,Yb}$ (2% at.) under excitation at: 3.77eV and 2.35eV (c). PL spectra of $\text{SnO}_2\text{:4%}$ thin film, excited with the multi-lines ultraviolet (3.53eV) of a Kr^+ laser, and of $\text{SnO}_2\text{:2%Er}$ pellet, excited with 2.57eV (482nm) from the same Kr^+ laser.

Fig. 2 – Photoluminescence of excitation for several compositions of Er doped SnO_2 xerogel at room temperature (0.1, 1, 2 and 4at% Er).. Emission is fixed at 1525 nm.

Fig 3 – PL spectra for $\text{SnO}_2\text{:0.5at%Eu}$ and $\text{SnO}_2\text{:1.0at%Eu}$ xerogels at 295K, under excitation with the fourth harmonic of a Nd:YAG laser (4.65eV). Inset - PL for $\text{SnO}_2\text{:0.5at%}$ under excitation with the same 4.65eV laser line and with 2.53eV line of an Ar^+ laser.

Figure 4 - Decay of photo-excited conductivity at several temperatures for (a) $\text{SnO}_2\text{:0.1at%Eu}$, (b) $\text{SnO}_2\text{:1at%Eu}$. (c) Resistivity as function of temperature for $\text{SnO}_2\text{:0.1at%Eu}$ and $\text{SnO}_2\text{:0.1at%Er}$ in the dark and long times after submission to the fourth harmonic of a Nd:YAG laser (4.65eV).

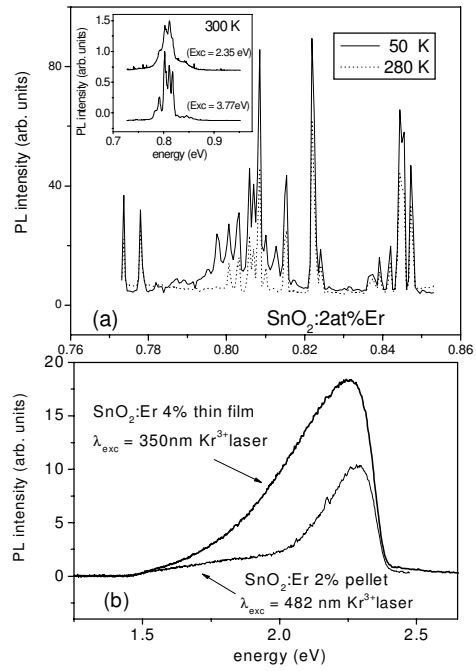


Figure 1

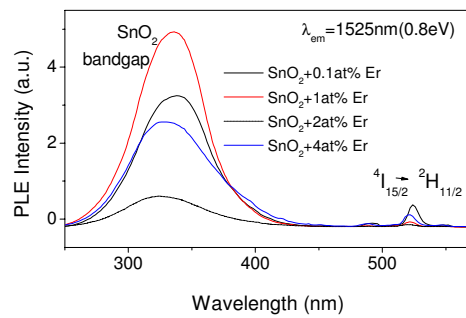


Figure 2

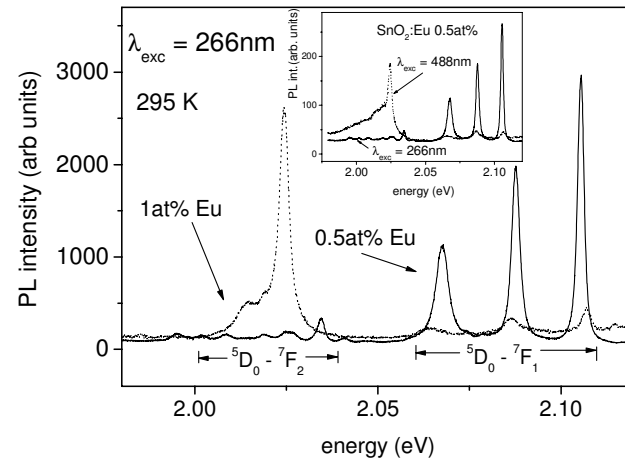


Figure 3

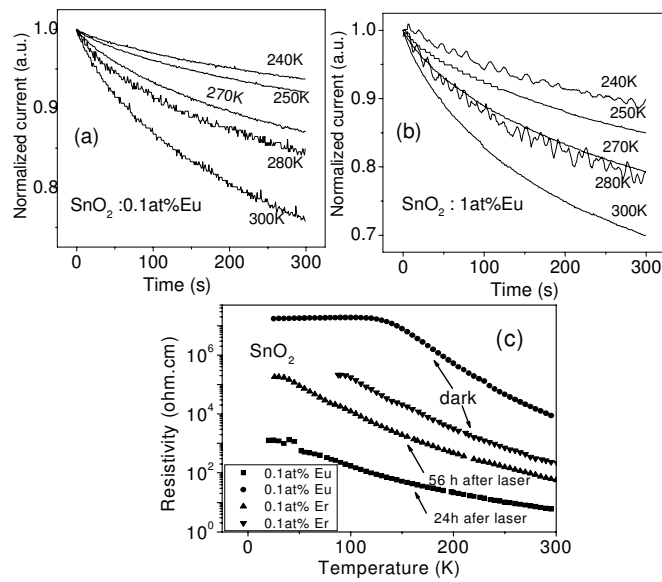


Figure 4