Ultraviolet Excitation of Photoconductivity in Thin Films of Sol-Gel SnO_2

L. V. A. Scalvi[a*], V. Geraldo[a,b], E A Morais[a], C. V. Santilli[c], P. B. Miranda[a], Tiago J. Pereira[a]

[a] Departamento de Física - FC - UNESP, C. Postal 473, 17033-360 Bauru - SP, Brazil

[b] Instituto de Física de São Carlos - USP, C. Postal 369, 13560-970 São Carlos - SP, Brazil

[c] Inst. Química de Araraquara - UNESP, C. Postal 355, 14801-907 Araraquara - SP, Brazil

Abstract

We have measured photoconductivity spectra for a large temperature range, of SnO_2 thin film using a deuterium source. The intensity of photocurrent spectra in the range 200-400nm is temperature dependent, and the photocurrent increases in the ultraviolet even for illumination with photon energies much higher than the bandgap transition. The explanation for these results is related to recombination of photogenerated electron-hole pairs with oxygen adsorbed at grain boundaries, which is consistent with a large amount of crystallites of nanometric dimensions inside the material. This high density of nanoscopic crystallites is obtained by evaluating peaks of X-ray diffraction data.

Keywords: Tin dioxide films; sol-gel; photoconductivity

* - corresponding author: Tel +55 14 3103 6084; FAX +55 14 3103 6094

e-mail: scalvi@fc.unesp.br

1. Introduction

Tin dioxide (SnO_2) is a wide bandgap semiconductor (forbidden gap in the range 3.5-4.0 eV [1]). When undoped, it presents n-type conduction due to oxygen vacancies and interstitial tin atoms. In the form of thin films, this material is characterized by high optical transmission [2]. The conjunction of optical and electrical properties make tin dioxide very attractive for many kind of applications in opto-electronic devices [3], gas sensors [4,5] and solar collector [6]. SnO_2 film properties are strongly influenced by preparation technique. The sol-gel route for obtaining SnO_2 thin films presents many advantages compared to other technique, such as excellent homogeneity, thickness control and possibility of coating large and complex surfaces, using both inorganic and organic precursors. However the electrical properties of layers prepared by this sol-gel process are worse compared to films deposited by other techniques. This worse performance is generally attributed to a combination of effects associated to grain dimensions of sol-gel materials. As shown in this paper, crystallites generated by our sol-gel dip-coating route have nanoscopic dimensions. Therefore a considerable amount of crystallites is present in the material, which makes electron scattering at grain boundaries, the most relevant mechanism to the film conductivity. Moreover, the presence of oxygen ionic species adsorbed at grain boundary may create a depletion layer as large as half of grain width [7]. The physics of electronic conduction in these films is peculiar and rather unknown. Therefore, it deserves a careful investigation.

In this work, we present new results concerning the electrical transport in nanocrystalline undoped SnO_2 thin films. Photocurrent spectra are obtained by using a deuterium source to excite the sample in the ultraviolet range, at low temperature. Spectra are normalized concerning the film optical absorption and the photon flux reaching the sample. The net result is the photoconductivity quantum yield, which shows marked temperature dependence.

2. Experimental

Colloidal suspensions of SnO_2 nanoparticles have been prepared from Sn^{4+} aqueous solution (0.25 mol.l^{-1}) obtained by dissolution of $SnCl_4.5H_2O$. Hydrolysis was promoted by addition of ammonium hydroxide (NH_4OH) under magnetic stirring until pH reaches 11. The precipitated obtained by this way was submitted to dialysis in order to eliminate as much as possible chloride and ammonium ions. These suspensions were used for film deposition on silicate glass substrates by dip-coating technique, with a withdrawing rate of 10 cm/min. After each dip, the deposited film is fired at 400^{o}C for 10 min. When the number of 30 layers is reached, films are annealed at 550^{o}C for 1 hour in air.

To perform electrical measurements, Indium electrodes have been evaporated on the samples through a shadow mask in an Edwards evaporator system. Electrodes are annealed to 150^{o}C for 20 min in air. Low temperature electrical measurements were done in an Air Product Cryostat that controls temperature in the range 25-300K to within 0.1K.

For photoconductivity (pc) spectrum measurements, illumination was provided by a 30W deuterium lamp. A computer controlled ultraviolet monochromator selects the excitation wavelength. The photocurrent is continuously recorded by the computer through a 6517A Keithley electrometer. The normalization procedure eliminates the dependence of the pc excitation upon the incident light intensity and sample absorption coefficient, so that the pc quantum yield is proportional to the product of carrier photogeneration efficiency, mobility and time.

For X-ray diffraction measurements it was used a Rigaku diffractometer coupled with a Cu source of 40kV and 20mA of current. Detector rate is 3 degree per minute with a 0.02-degree step.

3. Results and Discussion

Figure 1 shows the room temperature photoconductivity (pc) quantum yield in the range 200-400 nm for an undoped SnO_2 thin film. The inset in figure 1 shows excitation intensity spectra, which is measured with a Si photodetector coupled to a lock-in amplifier.

As it can be seen in figure 1, the pc quantum yield increases from 350nm and keeps increasing until about 220 nm. The measured photocurrent at room temperature is of order of μA. The variations in excitation intensity have no influence on the pc quantum yield, as it can be easily seen by comparing its shape with the incident intensity spectrum in the inset of figure 1. The shoulder about 265 nm in the quantum yield, can not be associated to a peak in the lamp spectrum, since the influence would be much more pronounced in the range 300-400nm, which is not observed.

The photoconductivity (pc) quantum yield is given by:

$$\text{PC Quantum Yield} = I_{pc} / (\text{Abs} \cdot N_{ph}) \qquad (1)$$

I_{pc} is the photocurrent measured in Amps, Abs is the film absorbance spectrum and N_{ph} is the number of photon reaching the sample as function of wavelength of irradiating monochromatic light. N_{ph} can be obtained by taken into account the light that effectively reaches the film, measured by a photodetector placed at same position of the film in the optical setup, divided by the detector response and the energy of illuminating monochromatic light. The PC Quantum Yield may be interpreted as the measured photocurrent normalized by the number of photons effectively absorbed by the film.

Figure 2 shows the pc quantum yield for several temperatures. The main figure 2 shows the result for 200K and the superior inset in figure 2 displays photocurrent measurement for 100 K and 70 K. They are shown separately for better comparison due to quite different magnitude. The lower the temperature, the lower the photocurrent signal, in good agreement with electron capture with decreasing temperature, typical semiconductor behavior. The shoulder located at 265 nm, observed at room temperature, becomes a peak when the temperature is decreased. The low power of the deuterium source (30 W prior to monochromator, on the order of μW at the sample) does not allow the conductivity to increase very much. In figure 2 we show only the spectra in the range 200-300 nm, since at these lower temperatures, the low magnitude of measured current, combined with the low absorption coefficient of the samples in the range 300-400 nm, lead to artifacts on the pc quantum yield due to normalization procedure for wavelengths longer than 300nm. The lower inset in figure 2 shows the effect of illuminating the undoped SnO_2 film with the fourth harmonic of a Nd:YAG pulsed laser (266nm), at 120 K. The pulsed laser is irradiated onto the sample though quartz windows. The pulse duration at 266nm is about 6

ns and the pulse energy is 4,8mJ. The pulse repetition rate is 10 Hz. Although we have published a temperature dependent study of laser excitation on sol-gel SnO_2 films previously [8], this result was reproduced here for sake of clarity, since it is an important ultraviolet excitation result related to these films. Besides it helps the understanding of photoconductivity spectra reported in this paper. The conductivity increases up to one order of magnitude under laser excitation, until saturation, and remains constant after the illumination is removed.

With the normalization provided on the photocurrent by the pc Quantum Yield calculation, the dependences of the pc excitation spectrum of figures 1 and 2 upon both the spectrum of the incident light reaching the sample and the undoped SnO_2 optical absorption spectra are removed. Therefore changes in the pc quantum yield may be interpreted as due to variation of photogenerated carrier density, mobility and/or lifetime. The gradual increase in the pc quantum yield for excitation wavelengths below 300nm, may be associated with changing carrier concentration and mobility in these films. The enhanced conductivity results from variation of free electron density plus decrease of space charge layer at grain boundaries. Both effects are related to releasing of adsorbed oxygen, which is removed from the chamber by vacuum pumping. The system is kept under 10^{-5} Torr of pressure and the amount of gaseous oxygen available to react with free electrons is reduced. This participation of oxygen in the recombination becomes evident when we consider that even far from the bandgap transition (3.5-4.0 eV) the light energy keeps promoting the conductivity increasing. If the increase of conductivity were only due to electron–hole pair excitation, the recombination of these charge carriers for illumination with energies rather above the bandgap transition should decrease the conductivity. Besides the excitation system has intensity practically negligible at short wavelength range. The observed behavior must include electron and hole trapping by oxygen species since desorption and adsorption are slower process than electron-hole recombination, because they depend on atomic diffusion into the sample (which is helped by the porosity of this material – 33%) and displacement of gaseous oxygen along the surface. Even though an influence of the normalization procedure may not be discarded, such an ultraviolet band deserves a deeper investigation and therefore, we shall continue our photoconductivity spectrum using more intense tunable UV light sources. The lower inset in figure 2 show the slow increase of

conductivity upon illumination of the SnO_2 film. We note that keeping the temperature constant and removing the illumination leads to a practically constant conductivity value - persistent photoconductivity (PPC) [8-10]. Conductivity varies again only when temperature is increased, but the room temperature value is recovered only a few hours later. The explanation of this PPC effect is related to recombination of adsorbed oxygen with photogenerated electrons and holes[8]. Although the higher conductivity is a metastable effect caused by intense laser illumination, when light is removed the conductivity does not return to its original value because the oxygen released from the film is continuously eliminated by vacuum pumping. This is also observed in the photoconductivity spectra, since the high conductivity value does not decrease even for illumination energies much higher than the bandgap transition.

The peak observed in the PC quantum yield at low temperature, shown in figures 1 and 2, located about 265 nm is a striking result since it coincides with the excitation wavelength that induces PPC in undoped SnO_2 sol-gel films. The effect of decreasing PC quantum yield intensity with temperature means that carriers are much more efficiently grounded to donor levels and the low light intensity is not enough to excite high photoconductivity effect. The much more intense laser light excitation confirms it, since induces high conductivity for lower temperature, as we have concluded previously [8].

Figure 3 shows X-ray diffraction data for this film. Comparing these results with cassiterite pattern [11], there is good agreement as indicated by crystal directions labeled in figure 3. The average particle size can be determined from diffraction peaks and for the main directions, indicated in figure 3, the average particle size is given in table 1.

Table 1 – Average particle size of undoped SnO_2 thin film

Direction (hkl)	***Particle size (nm)***
(110)	4.7
(101)	6.0
(211)	4.7

The quite small size of these crystallites (nanoscopic dimensions) leads us to believe that grain boundary scattering is the most relevant mechanism for film conductivity.

Previously [12,13] we have reported that this scattering phenomena is responsible for the high resistivity of films grown by this method. Besides, the large amount of crystallites is concomitant with high possibilities of oxygen adsorption at grain boundaries and may explain the observed phenomena reported here.

4. Conclusion

Variation of photoconductivity with excitation wavelength is measured using a deuterium source. These spectra are measured for the first time as function of temperature. Normalization by the photon flux reaching the sample, leads to increasing photocurrent for illumination with monochromatic light of increasing energy. The photocurrent quantum yield has an onset at the absorption edge and continues to increase even for photon energies much higher than the bandgap transition. This phenomenon is related to electron and hole recombination with adsorbed oxygen. We also reproduce persistent photoconductivity phenomenon in undoped SnO_2 thin film, in order to clarity the result shown in this paper. We interpret this phenomenon as also related to recombination of photogenerated electron-hole pairs with adsorbed oxygen.

X-ray diffraction data yields nanocrystallites with average size of about 5 nm. This result explain the high resistivity of films grown by sol gel dip coating and the high probability of oxygen absorption at grain boundaries, since the whole film has a high concentration of dangling bonds at crystallite interfaces.

Acknowledgments

The authors wish to thank Prof. Ligia O Ruggiero and Margarida J. Saeki for the help with the technical set-up, and CAPES, FAPESP, CNPq and MCT - PRONEX for the financial resources.

References

1.Ray, S C, Karanjai, M K and Dasgupta, D, Tin dioxide based transparent semiconducting films deposited by the dip-coating technique, *Surface & Coatings Technol.*, 1998, **102** 73-80

2.Dien, E., Laurent, J. M., Smith, A., Comparison if Optical and Electrical Characteristics of SnO_2 – based Thin Films Deposited by Pyrosol from Tin Precursors, *J. European Ceramic Society,* 1999, **19,** 787 – 789

3. Terrier C., J. P. Chatelon and Roger, J. A. , Electrical and optical properties of Sb:SnO2 thin films obtained by the sol-gel method, *Thin Solid Films*,1997, **295**, 95-100

4. Guglielmi, M, Menegazzo, E., Paolizzi, M., Gasparro, G., Ganz, D., Putz, J. and Aegerter, M A., Sol-gel deposited Sb-doped tin oxide films, *J. Sol-Gel Sci. Technol.,*1998, **13,** 679-683

5. Nakata S. and Ojima N., Detection of a sample gas in the presence of an interferant gas based on a nonlinear response, *Sensors and Actuators* 1999, **B 56,** 79-84

6. Sanon G., Rup R. and Mansingh A., Band-gap narrowing and band structure in degenerate tin oxide (SnO_2) films, *Phyical. Review B* , 1991, **44**, 5672-5680

7. Watson J., Ihokura K. , Coles G.S.V., The tin dioxide gas sensor, *Meas. Sci. Technol.*, 1993, **4**, 711-719

8. Morais, E. A., Scalvi, L V A, Geraldo, V., Scalvi, R M F. Ribeiro, S. J. L., Santilli, C. V. and Pulcinelli, S H., Electro-optical properties of Er-doped SnO_2 thin films, *J. European Ceram. Soc*., 2004, **24**, 1857-1860

9. Mooney P.M., Deep Donor Levels (DX Centers) in III-V Semiconductors, *J. Appl. Phys*. , 1990, **67** ,R1-R26

10. Ghosh S. and Kumar V., Confirmation of metastable neutral DX^0 state of Si-related DX center in $Al_xGa_{1-x}As$ by transient photoconductivity, *Solid State Comm*., 1997, **104** , 781-785

11. Powder Diffraction File, Inorganic, vol. 21, Pub. By the JCPDS, Swathmore, 1983

12. L. V A Scalvi, F. R. Messias, A. E. Souza, M. Siu Li, C. V. Santilli and S.H. Pulcinelli, Improved conductivity induced by photodesorption in SnO_2 thin films grown by a sol-gel dip coating technique, *J. Sol-Gel Sci. Technol,* 1998*,* **13**, 793-798
13. Messias, F.R., Vega, B A V., Scalvi, L. V. A., Siu Li, M., Santilli, C. V. and Pulcinelli, S. H., Electron Scattering and effects of sources of light on photoconductivity of SnO_2 coatings prepared by sol-gel, *J. Non-crystalline Solids*, 1999, **247**, 171-175

Figure Captions

Fig. 1 Photoconductivity excitation spectra for and undoped SnO_2 thin film at room temperature. Inset – excitation intensity spectra.

Fig. 2 Photoconductivity excitation spectra for and undoped SnO_2 thin film at 200 K. Superior Inset - Photoconductivity excitation spectra at 70 and 100 K. Lower Inset - Normalized conductivity as function of time of an undoped SnO_2 thin film, for excitation with the fourth harmonic of a Nd:YAG laser (266nm), at 120K.

Fig. 3 – X-ray diffraction data for undoped SnO_2 deposited by dip coating sol gel

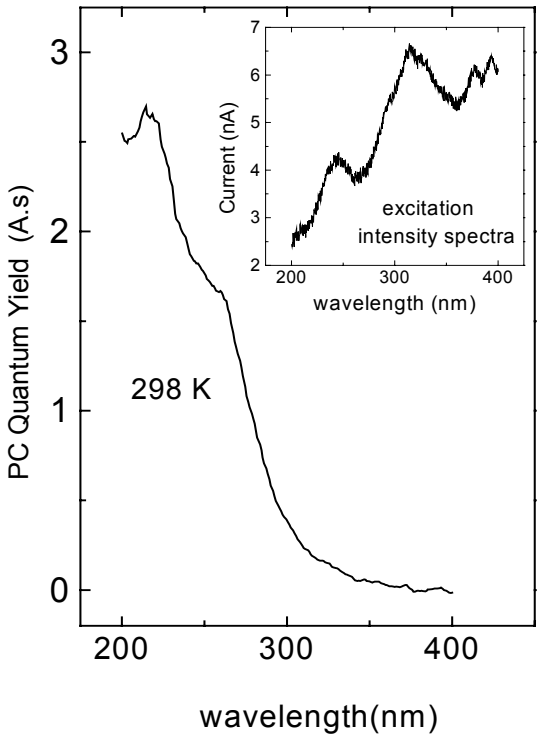
PC Quantum Yield (A.s)
wavelength(nm)
298 K
Current (nA)
wavelength (nm)
excitation
intensity spectra

Figure 1

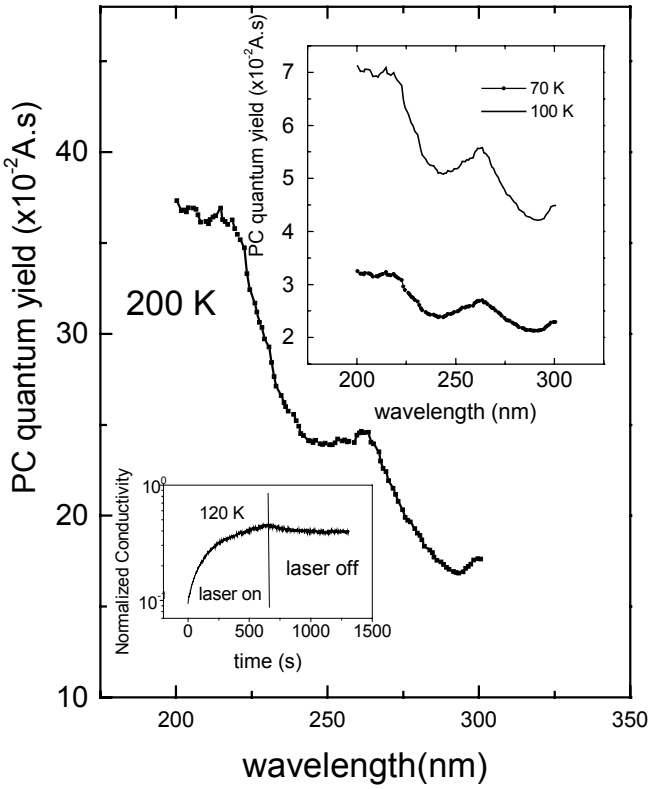

Figure 2

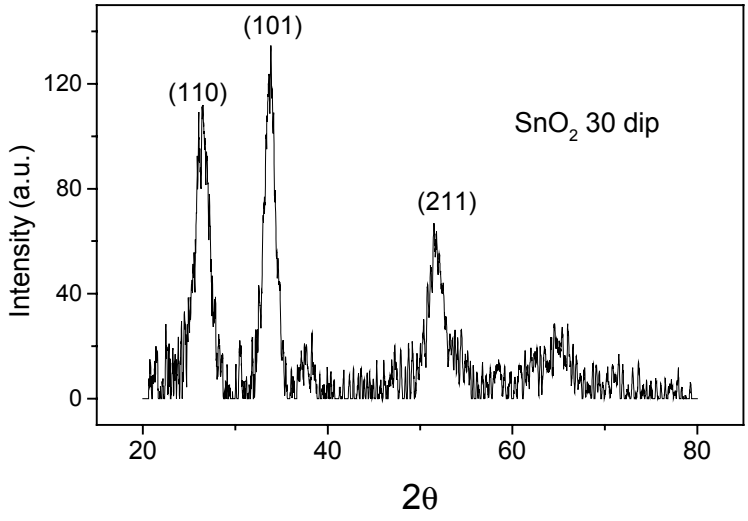

Figure 3