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Electro-optical properties of Er-doped SnO_2 thin films

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Abstract

Photoconductivity of SnO_2 sol-gel films is excited, at low temperature, by using a 266 nm line—fourth harmonic—of a Nd:YAG laser. This line has above bandgap energy and promotes generation of electron-hole pairs, which recombines with oxygen adsorbed at grain boundary. The conductivity increases up to 40 times. After removing the illumination on an undoped SnO_2 film, the conductivity remains unchanged, as long as the temperature is kept constant. Adsorbed oxygen ions recombine with photo-generated holes and are continuously evacuated from the system, leaving a net concentration of free electrons into the material, responsible for the increase in the conductivity. For Er doped SnO_2, the excitation of conductivity by the laser line has similar behavior, however after removing illumination, the conductivity decreases with exponential-like decay.
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1. Introduction

In the last decades, rare-earth doped semiconductor materials have obtained widespread interest, since they can contribute for technological innovation and development of new optoelectronic devices. Er^{3+} ion present several radiative transition concerning decay from several excited core levels to ground state, yielding emission from visible to infrared. Particularly the 4f transition at about 1540 nm coincides with minimum absorption of fiber optics,[1] being of great interest for optical communication. On the other hand, tin dioxide is a wide bandgap semiconductor (3.5–4.0 eV),[2] which has been widely applied due to its physical and chemical properties. Doped SnO_2 thin films are characterized by high electrical conductivity, transparency of about 80–90% in the visible and high reflectivity in the infrared.[2] Undoped SnO_2 is an n-type semiconductor since oxygen vacancies or interstitial Sn^{4+} are donor sites. In the case of sol-gel films, crystallites are rather small (3–10 nm)[3] and a lot of oxygen is adsorbed at boundary layer, trapping electrons from the conduction band.[4] Then conductivity can be greatly increased by eliminating oxygen from boundary layer, which can be done by annealing at proper temperature and gas composition of the annealing chamber.[5] Er^{3+} is expected to be an acceptor in SnO_2 since when it substitutes Sn^{4+} in the cassiterite structure, removes an electron from valence band, leaving a hole, which may recombine with a free electron. The main goal of our investigation is doping with optically active elements a highly transparent matrix, for production of devices with low optical loss. In this case Er^{3+} doped SnO_2 thin film finds potential application in integrated optics amplification devices.[6]

In this work we present photoconductivity excited by a 266 nm line for undoped and Er-doped SnO_2 thin films. These results may bring new light on electrical transport properties of nanocrystalline tin dioxide and the development of new electro-optic switch.

2. Experimental

Colloidal suspensions were prepared by sol-gel process described in detail elsewhere.[3] To an aqueous solution of $SnCl_4.5H_2O$ (0.2 M l^{-1}) the desired amount of $ErCl_3.6H_2O$ was added, under magnetic stirring, followed by addition of NH_4OH until pH reaches 11.

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Then the suspension was submitted to dialysis against distilled water by approximately 10 days in order to eliminate Cl^- and NH_4^+ ions. This procedure leads to stable and transparent SnO_2:Er aqueous sol, which were used for film deposition on silicate glass substrates by dip-coating technique, with a withdrawing rate of 10 cm/min. Multi-dipped films were continuously deposited at room temperature with a little interruption after each dip, in order to fire the film at 400 °C for 10 min. When the number of layers reached 30, resulting film was annealed at 550 °C for 1 h. The resulting thickness evaluated from scanning electron microscopy was about 200 nm.

To perform electrical measurements, In electrodes have been evaporated on the samples through a shadow mask in an Edwards evaporator system. Electrodes are annealed to 150 °C by 20 min in air. Low temperature electrical measurements were done in an Air Product Cryostat that controls temperature in the range 25–300 K within 0.1 K of precision. The fourth harmonic of a Nd:YAG pulsed laser is irradiated onto the sample though quartz windows. The pulse energy at 266 nm is 4.8 mJ. The used frequency is 10 Hz.

3. Results and discussion

By illuminating SnO_2 films at low temperature, we have found an effect known as persistent photoconductivity (PPC). Although for SnO_2 this phenomenon has its origin rather different from what happens in other semiconductor materials such as $Al_xGa_{1-x}As$,[7,8] the effect is essentially the same. Fig. 1 shows normalized resistivity as function of time for an undoped SnO_2 film, irradiated with the fourth harmonic of a Nd: YAG pulsed laser, coupled with doubling crystals (266 nm), at low temperature. The resistivity decreases up to 40 times under this excitation, until saturation. It is interesting to notice that the lower the temperature, the higher the variation in conductivity (resistivity decreases). This effect is related to electron mobility in SnO_2 sol-gel film, which is dominated by grain boundary scattering, and its dependence with temperature[9] goes with T^{-1}. Although there is other competing electron scattering mechanisms, such as ionized impurity and polar optical, the huge amount of crystallites in these sol-gel films, concomitant with oxygen desorption at grain boundary, makes grain boundary scattering the most relevant mechanism.[10] Then it seems that laser irradiation releases about the same amount of free electrons, independent of temperature, and the dependence with temperature of resistivity variation, observed in Fig. 1, is related to variation on electronic mobility. When illumination is removed, the conductivity remains practically unchanged, as long as the temperature is kept at constant value. Conductivity varies again only when temperature is increased, however film recovers its room temperature resistance after a few hours.

The fact that sample resistance returns to its original room temperature value discards permanent effects in the SnO_2 film structure such as increase in crystallinity, which could be caused by laser heating. The explanation of this PPC effect is related to recombination of adsorbed oxygen with electron and holes generated by illumination with above bandgap light, which makes possible the following reactions:[5]

$$1/2\ O_2 + e^- + SnO_{2-x} \rightarrow O^-_{ads}(SnO_{2-x}) \quad (1)$$

$$h^+ + O^-_{ads}(SnO_{2-x}) \rightarrow 1/2\ O_2 + SnO_{2-x} \quad (2)$$

where SnO_{2-x} is the non-stequiometric tin dioxide film and $O^-_{ads}(SnO_{2-x})$ means the adsorbed negatively charged oxygen atom.

During illumination, although both reactions take place simultaneously, the first one occurs with less intensity since the system is under vacuum (about 10^{-5} Torr) and then the available amount of gaseous oxygen decreases. As a general consequence, an increase in the free electron concentration in the sample is observed, resulting in increase on SnO_2 film conductivity. Although the higher conductivity is a metastable effect caused by intense monochromatic light irradiation, when laser illumination is removed, conductivity does not return to its original value because the oxygen released from the film is continuously eliminated by the vacuum pumping which decreases the probability of occurring of Eq. (1). Another point towards this

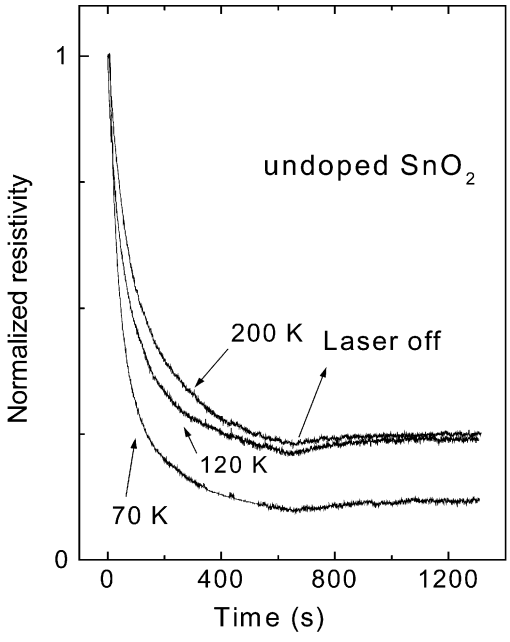

Fig. 1. Normalized resistivity as function of time for a undoped SnO_2 film, excited with a 266 nm line of a pulsed Nd:YAG laser coupled with doubling crystals.

recombination between charge carriers and oxygen adsorption is the little influence of laser pulse frequency on photoconductivity excitation. Although this frequency is rather low, 10 Hz, no oscillation on photoconductivity is observed, which means that we are facing a cumulative effect, in good agreement with our hypothesis, since recombination with oxygen depends on atomic diffusion into the sample and motion rates of gaseous oxygen on the surface, being a much slower process than electron-hole recombination. Besides the gaseous specimens are continuously eliminated.

Fig. 2 shows the same kind of experiment for a SnO_2:4%Er sample. Below 100 K, illumination removing does not lead the film to PPC effect, but to a decrease in conductivity as function of time. It is important to observe the very high resistivity value of Er-doped SnO_2 film. A similar result has been obtained for Eu-doped SnO_2 powder.[11] This is an evidence of acceptor-like character of Er^{3+} in SnO_2, since the n-type conduction of undoped SnO_2 film is greatly compensated by Er^{3+} introduction.[12] The decay in photoconductivity is another evidence of this acceptor-like behavior, since the conductivity reached by illumination is not maintained when irradiation is stopped (absence of PPC). Then the laser line has energy enough to excite bandgap transition and Er^{3+} ions present into the sample. When illumination is removed, the acceptor-like nature of these defects leads to electron trapping, whose time-dependent behavior is as shown in Fig. 2. It also must be mentioned that the solubility limit of tripositive rare-earth ions in SnO_2 is known to be about 0.05% and the excess ions are supposed to be segregated at grain boundaries.[13] It is not possible at this moment to separate trapping contributions from Er^{3+} substitutional ions or segregated at boundary layer.

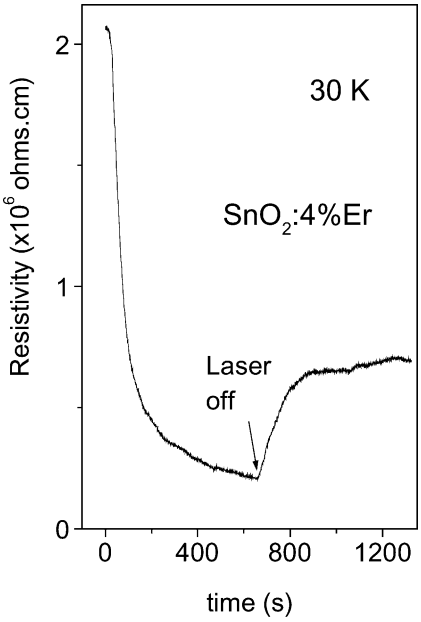

Fig. 2. Resistivity as function of time for a SnO_2:4%Er film, excited with a 266 nm line of a pulsed Nd:YAG laser coupled with doubling crystals.

Fig. 3 shows absorption spectrum from undoped SnO_2 film, obtained subtracting measured data of deposited film on silicate glass from absorption substrate data. The inset in Fig. 3 shows absorption spectrum from undoped SnO_2 solution (before film deposition) and SnO_2:4%Er deposited on quartz substrate. Although glass absorption is well known to take place below 300 nm, all these curves assure that at laser excitation wavelength (266 nm) also the SnO_2 film is absorbing. Then, at 266 nm there is absorption from SnO_2 film as well as from the silicate glass substrate. However only the film has trapped carriers to be released by light irradiation, in order to increase the conductivity. Besides the In contact only diffuses a little into the film, when annealed. It is hard to believe that annealing at 150 °C would lead to a In diffusion that could reach the substrate or even the interface substrate-film. Therefore, we believe that the observed phenomena, reported in this paper, comes from the film itself.

Fig. 4 shows the decay for two different temperatures. The lower the temperature, the higher the conductivity, which means that even for Er-doped films, the grain boundary scattering is the most relevant mechanism. However we have not found yet a temperature dependence of decay rate, since the variation between the curves shown in Fig. 4 is quite low, and hard to distinguish for intermediate temperatures. Then a further investigation of temperature dependence of transient decay of persistent photoconductivity is under progress and shall be published soon. These results will yield important parameters of electron trapping by Er^{3+}-like defects such as capture cross section, which can be deduced from an Arrhenius plot of the linear portion of the temperature dependent transient decay of PPC.[14]

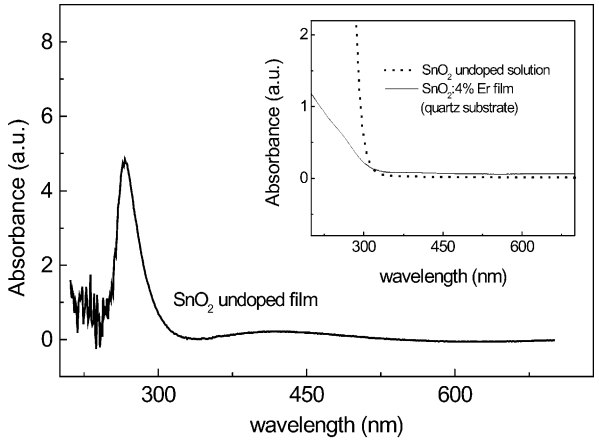

Fig. 3. Absorbance of SnO_2 undoped film on silicate glass substrate. Data are obtained subtracting absorbance of deposited film from substrate absorbance. Inset—absorbance of SnO_2 undoped solution and SnO_2:4%Er on quartz substrate.

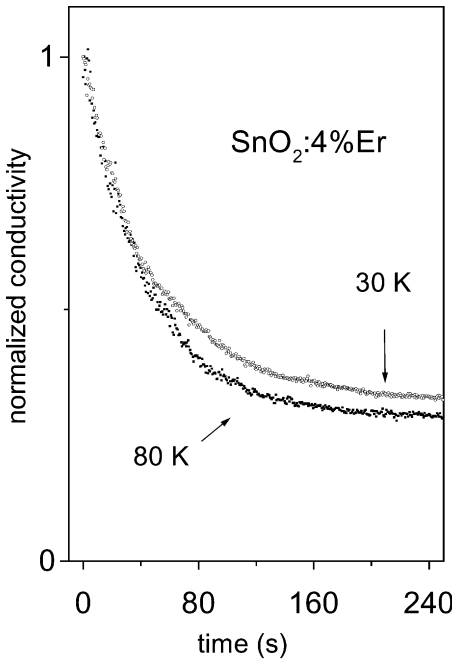

Fig. 4. Normalized conductivity decay for SnO_2:4%Er film at 30 and 80 K.

4. Conclusion

We have found persistent photoconductivity at low temperature in undoped SnO_2 thin films deposited through sol-gel process, for the first time. This effect is related to recombination of photogenerated electron-hole pairs with adsorbed oxygen.

In Er-doped SnO_2 thin films persistent photoconductivity is not observed, instead an exponential-like decay of conductivity takes place when illumination is removed. Although this decay below 100K seems to be temperature dependent, the complete set of decay measurements as function of temperature is under progress and the modeling will yield the capture cross section by Er related centers present in this material.

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