Low temperature thermally stimulated current analysis of nanocrystalline Titanium dioxide

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Lattice disorder represents a limiting factor for the operative performances of semiconductor-based devices. For this reason investigation of microscopic disorder is strategic in many fields of application. Here we present a method, based on decayed Thermally Stimulated Current measurements, able to resolve the shape of the Density Of States (DOS) close to extended band levels. The technique has been applied to nanocrystalline TiO_2, a material of growing interest for applications in new generations of photovoltaic systems. Our results show that, due to the high level of disorder, the DOS is characterized by an exponential distribution with a tailing parameter of 53.5meV.

1.Introduction

Nanocrystallyne Titanium dioxide (nc-TiO$_2$) is a material of growing interest in several application fields, ranging from catalysis to solar energy conversion. In Dye Sensitized Solar Cells (DSSCs) [1] it is used as the semiconducting medium at the negative electrode. Investigation of defect states and of their influence on electrical transport properties of nc-TiO$_2$ films is strategic in the perspective of increasing the efficiency of DSSCs beyond the present values, now limited to 12% [2]. In fact nanoparticles are characterized by a great number of defects and this disorder influences the Density Of States (DOS) in the nearby of the conduction/valence band edges. An intragap DOS characterized by exponential tails, below (above) the conduction (valence) band, has been hypothesized also for nc-TiO$_2$ films [3] in accordance with that usually found in disordered and amorphous materials.

This work is aimed at investigating the DOS structure of nc-TiO$_2$ by means of decayed Thermally Stimulated Current (TSC) technique [4][5][6], priming the sample with UV light. TSC spectroscopy, originally developed for characterization of isolated intragap defect states, can be properly adapted for a continuous distribution of energy levels and allows one to establish a relationship between the collected charge and the defect concentration. In this case, the technique has been applied to the temperature range where shallower defects emit, i.e. between liquid He temperature and room temperature (RT), in order to study the DOS close to the conduction/valence band edges.

2.Materials and methods

To manufacture samples we used a commercial colloidal system, specifically developed for prototypal electrodes in DSSCs (Solaronix, Ti-nanoxide D), containing about 11 % wt. nc-TiO$_2$ (in anatase phase), with particles size dispersion in the range 13-400 nm. We deposited the nc-TiO$_2$ paste on an alumina substrate having two parallel gold contacts, 7mm long and spaced 0.8mm. In order to remove the solvent ,the deposition has been syntherized in two steps, 30 minutes each, first at 280 °C and then at 450°C. At the end of the process we got a nanoporous film about 1 μm-thick.

Current-voltage characteristics of the sample, measured at room temperature, are shown in Fig. 1 . They display an ohmic behaviour in the overall range. Due to the wide bandgap (~3.2eV) of TiO$_2$, the intrinsic concentration of carriers at room temperature is very low, so the current of our sample is in the pAs range. In the following TSC measurements we apply a bias of 100V across the sample, in view to get an electric field of about 10^5 V/m , i.e. of the same order of that present in a typical DSSC.
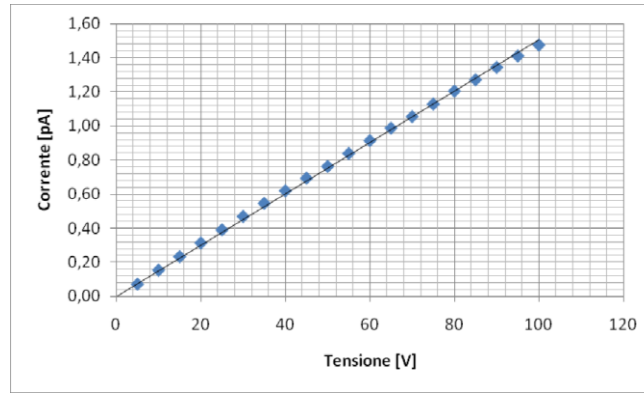
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Figure 1 Room temperature I-V characteristic of a nanostructured TiO$_2$ film with planar Au contacts.

To perform TSC measurements the alumina substrate coated with the nc-TiO$_2$ has been placed in a sample holder equipped with a 4Ω heating resistor and a silicon temperature sensor. The sample holder has been inserted within a dewar containing liquid He (LHe) and positioned over the LHe vapours, to ensure stable temperatures down to 4.2K, minimize thermal inertia and reduce possible mismatch between the sample and the thermometer.

Polarization of the sample and current reading was performed by a Keithley 6517 electrometer, the heater was biased by a TTi QL564P power supply and temperature was read by a Lakeshore DRC91C temperature controller. All instruments were controlled by a PC through the GPIB interface using Matlab (The MathWorks, Inc.). Priming was performed by a CW UV-LED (355nm , i.e. 3.49 eV, 8.4 mW power) placed in front of the sample inside the film holder.

3. Experimental Procedures

In quasi-equilibrium hypothesis and first order kinetics the Thermally Stimulated Current spectrum due to a single defect is given by :

$$I_{TSC} \propto e_n(T)N_t \exp\left[-\frac{1}{\beta}\int_{T_i}^{T_f} e_n(T)\cdot dT\right] \qquad (1)$$

with N$_t$ defect concentration, β constant heating rate and $e_n(T) \propto T^2 \exp[-E_t/(KT)]$ emission coefficient. During a TSC scan, the shape of the spectrum is initially dominated by the exponential rise, due to e$_n$(T): on this effect is based the *initial rise* method [7], widely used to determine the activation energy E$_t$, i.e. the energy of an intragap level due to the defect. The total charge collected during the TSC scan is then proportional to the defect concentration. In case of disordered materials, where a continuous distribution of levels will participate to the TSC, a more detailed analysis is needed. In fact, as shown in ref. [4] the DOS reconstruction requires not a single TSC scan, but a full set of contiguous TSC scans. Our experiments then proceeded as follows: first, the sample was primed with the LED, at temperature T$_0$, for about

10 minutes, biasing at 100 V . Then, holding the sample in the dark at the same temperature T_0 during 10 minutes, the fast transient effects were relaxed. After that, the fractional TSC measurement started: the sample was heated up to a first maximum temperature T_{stop1}, then it was cooled down to a first minimum temperature T_{start1}, then heated again, and so on up to RT (see Fig.2 top). For each scan , from the recorded TSC, we then extracted the activation energy E_{act} (determined with the initial rise method) and the emitted charge Q calculated by integrating the current (Fig.2 bottom).
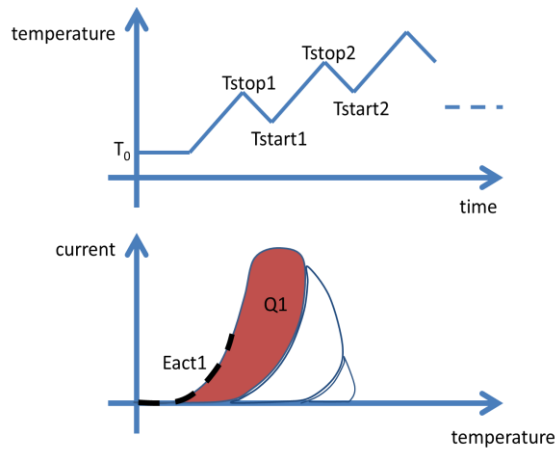

Figure 2 sketch of the decayed TSC method used to get charge vs. activation energy. The temperature is raised and lowered by steps (top). At each step the activation energy and the charge (red area) are computed (bottom).
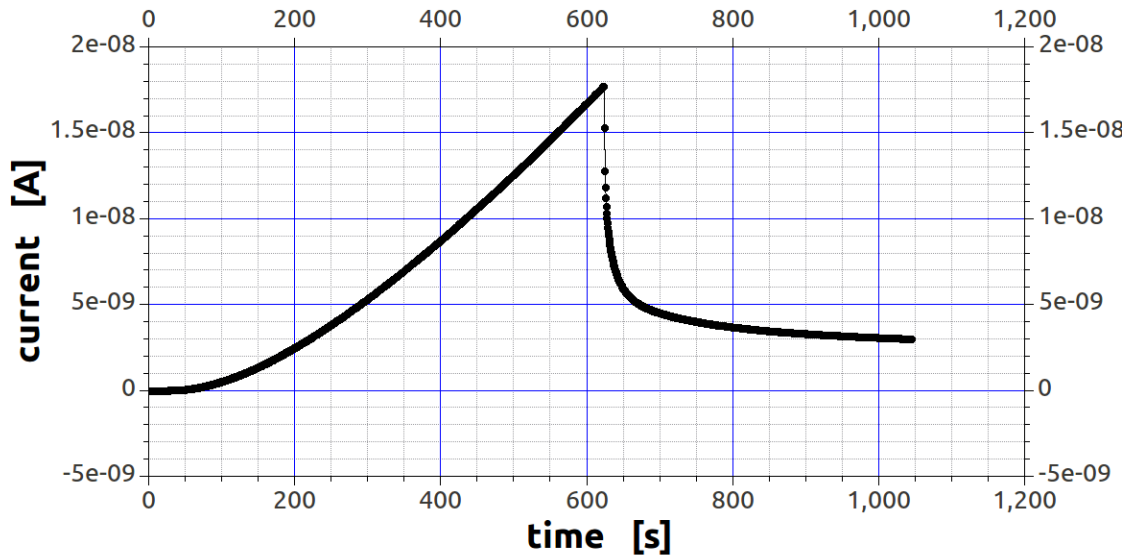
The decayed TSC technique is a powerful tool to resolve defects present in a broad band. With this method, by a progressive depletion of the emitting levels with the contiguous TSC scans it is possible to relate the number of states , proportional to Q, to the activation energy, and then to reconstruct the DOS [7]. A variant of the method was performed by Weise et al. [5] through a temperature scan followed by a heating up to the maximum temperature (about RT) at each step, the priming being performed before each step. In this manner he left out the uncertainty due to defects emitting at higher temperatures. Here, we assume that this charge is frozen and does not influence significantly the activation of the current from the investigated defect.

3.Experimental results

Fig. 3 shows the photocurrent transients at 10K obtained during illumination with the UV LED: we observe that the photocurrent do not reach a saturation, moreover a persistent current is present after the priming source is switched off.

Figure 3 Photocurrent transient obtained at 10 K illuminating the TiO2 sample with a 355 nm UV LED, applying a bias of 100V.
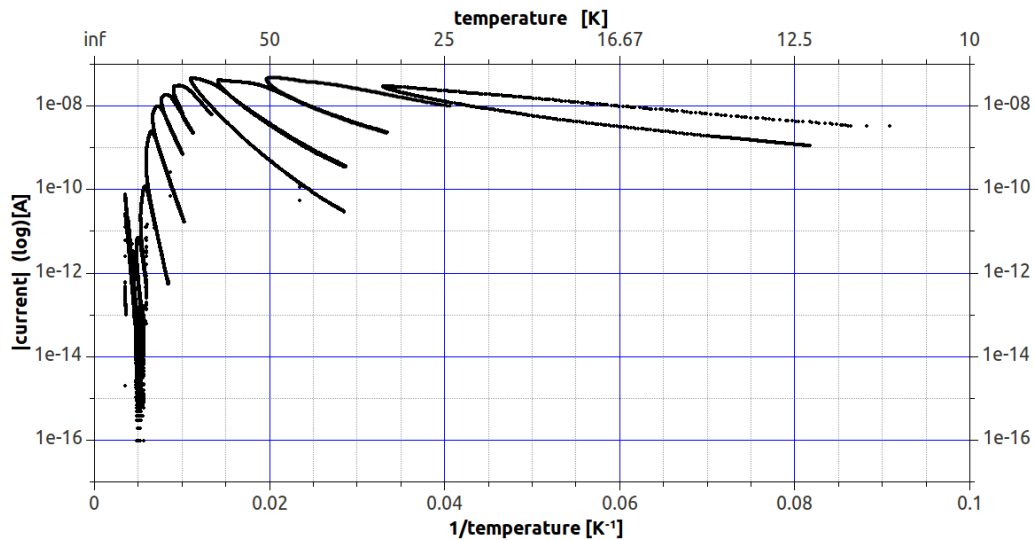

Figure 4 Arrhenius plot of the decayed TSC measurement after priming the sample at 10 K with a 355nm LED for 10 minutes (see Fig. 3). The bias voltage is 100V, temperature steps between consecutives scans are 20K (10K at very high temperature to increase the resolution).

Decayed TSCs after priming with UV-LED are shown in Fig.4: measurements were performed at steps of 20K between consecutives scans.

In Fig. 5 we show the charge versus activation energy computed from these measurements. We observe that, in the energy range 0.035-0.500eV, charge depends

exponentially on the activation energy; below 0.035 eV the decrease in the collected charge is very likely due to a non complete filling of the energy levels near the band gap, so data must be handled with caution. The dashed line is an exponential fit to the experimental data ($Q \propto \exp(-E_{att}/E_0)$) and gives a tail parameter of $E_0 = 53.5$ meV.

Figure 5 Charge versus activation energy as determined from decayed TSC measurements after UV LED priming. Dashed line: exponential fit.

4.Discussion

The photocurrent shown in fig. 3 is characterised by a very slow rise-time and the non-attainment of a saturation level, indicating an high level of microscopic disorder. In addition, the dark current after an initially "fast" decay stabilize itself at an almost constant value. These results agree with photoconductive measurements performed by Nelson et al. [8][9] on similar anatase films at room temperature. This behaviour is not yet fully understood: conduction in nanoporous and disordered materials is a rather complex mechanism were charge transport through the extended states and, by hopping, through the localized ones, coexist with a relative weight that changes with band filling (i.e. the Fermi level position) and temperature. At low temperature and moderate band filling the conductivity is mainly due to hopping through the band tail states and it requires a non-trivial treatment; nevertheless the conduction keeps the characteristic of a thermally activated process as in the case of a single defect level. In this sense, at first approximation, we can still describe a single TSC scan as a process where the current is due to the carriers thermally released from a narrow band (of the order KT) around a given level. The activation energy and the total collected charge are then directly related to the energy and density of states of the level. An accurate description of a TSC in this kind of systems, still lacking, strongly exceeds the limits of this paper and will be given elsewhere; here we limit ourselves to indicate, according our model, a few points. In Fig. 3 the rising photocurrent comes from both free and hopping carriers; after the light is tuned-off the free carrier contribution rapidly decays and only the hopping carrier contribution is left, this latter decaying very slowly at low temperature. From the sequential TSC scans of Fig. 4 the activation energies and charges are measured allowing one to determine how the number of states varies with energy, i.e. the DOS shape.

Our measurements indicate that inside the band gap nc-TiO$_2$ has indeed an exponential DOS decaying with an energy constant $E_0 = 0.0535$ eV. It is worth to stress that, provided the DOS shape is exponential, the E_0 constant is not affected by a rigid shift of the activation energies. This exponential DOS is common for disordered semiconductors and it is consistent with theoretical and experimental results for similar materials [3] [10][11]. The tailing factor of 53.5 meV is in agreement with values measured in TiO$_2$, by means of more indirect methods, and ranging in between 50 and 100 meV. [12][13][14].
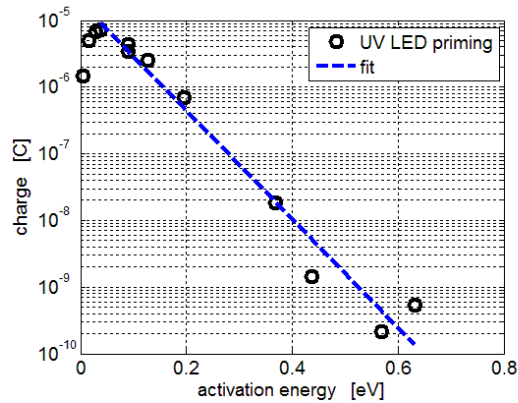
6. Conclusions

Nanocrystalline Titanium dioxide (nc-TiO$_2$) is a key material for the development of third generation solar cells: investigation of defect states and of their influence on electrical transport properties is strategic in the perspective of increasing the efficiency of new photovoltaic systems beyond present values. We investigated the defect structure of the shallower energy region performing thermal spectroscopy measurements in the range 10-300K.The decayed TSC method adopted in this study allowed for identifying the DOS even in a situation where the distribution is continuous and very broad. Thanks to this method, we showed that the DOS in the nearby of the conduction/valence band edges has an exponential shape with a tailing factor of 53.5 meV. The results still confirm that in inorganic semiconductors, as suggested by general models, disorder of any kind gives rise to intragap exponential tails [15][16]. In future, we plan to apply this technique to heavily irradiated semiconductors used as position detectors for high energy physics experiments, in view to get further information about the nature of their radiation damage under operative conditions.

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