

Correlation between simultaneous thermally stimulated conductivity and thermoluminescence transients-experimental case of stannic oxide monocrystals

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(Received 25 September 1978; accepted for publication 15 December 1978)

The general solution of thermally stimulated processes is known to need the complex formulation of a nonlinear functional. Classical solutions can yet be found in special cases of particular exchange mechanisms and using approximations. The implicit correlation between thermally stimulated conductivity (TSC) and luminescence (TSL) is an important element in the qualitative determination of the mechanism involved. In this paper we propose a method for deducing such information from a $\log(\text{TSC})$ -vs- $\log(\text{TSL})$ parametric plot. This method is expected to apply even in the complex situation of overlapping or low-level peaks. Typical cases are emphasized and an experimental illustration of the technique is proposed for stannic oxide monocrystals. The conclusions are shown to be in very good agreement with the results obtained from classical measurements of luminescence and photoconductivity.

PACS numbers: 78.60.Kn, 72.20. — i

In some previous papers¹⁻⁷ we have shown that the general solution of a problem of a thermally stimulated process (later referred to as TSP) must be expressed as a functional which can hardly be exploited due to its nonlinearity and nonstationarity. Nevertheless, explicit information can be found by using the correlation between the simultaneous transitory measurements of conductivity and luminescence.

Let us write the two essential equations in the classical form:

$$J_{\text{TSC}} = e\mu(T)En_c \{ T(t) \}, \quad (1)$$

$$J_{\text{TSL}} = k \frac{n_c \{ T(t) \}}{\tau_\lambda \{ T(t) \}},$$

where $\mu(T)$ is the mobility of the stimulated carriers, e is the electronic charge, E is the electric field (supposing an Ohmic process⁸ and $n_c \{ T(t) \}$ and $\tau_\lambda \{ T(t) \}$ are the functionals of $T(t)$ representing respectively the density of available conducting carriers and the coefficient of radiative recombination at wavelength λ .

It was, also, previously shown that eliminating $n_c \{ T(t) \}$ in the ratio $R = R_{\text{TSC}}/J_{\text{TSL}}$ leads to valuable information on the transient evolution of the density of recombination centers $m \{ T(t) \}$, corresponding to the emitted wavelength λ . The evolution of $m \{ T(t) \}$ is strictly characteristic of the mechanism of exchange of carriers between the localized traps and recombination centers and the delocalized states in the two bands.

The conclusions that emerge from various experimental situations explored such as in ZnS, ZnSe, AgBr, SnO₂,

and others was that a TSC or TSL relaxing system cannot be, in these cases at least, restricted to a two-level classical scheme but looks far more complicated because of the contribution of other simultaneous phenomena such as the release of holes into the valence band⁷ or ionic creation of recombination centers.⁶ One has, for instance, to examine very carefully⁹ the usually employed equation $J_{\text{TSL}} = -dm/dt$. Then, the functional approach^{3,7} of TSP must be considered as a powerful tool to improve the knowledge of the kind of mechanism involved which is a previous step before trying to develop a classical analysis¹⁰ of the glow curves and evaluating the parameters of the localized levels. Nevertheless, except for the case of very narrow peaks,⁶ the experimental processing of $R \{ T(t) \}$ needs to take into account the temperature dependence of a function $f(T) \sim \mu(T)/[\sigma_r(T)v(T)]$, where $\sigma_r(T)$ is the cross section for the radiative recombination and $v(T)$ is the thermal velocity.

This can only be done after a somewhat tricky experiment of fractional thermal emptying: such an experimental process obviously needs large amplitudes for the detected TSC and TSL peaks.

The purpose of the present paper is to propose another way to reach conclusions, even in the usual case of complex overlapping low-level glow curves. These conclusions are only qualitative, but help in suggesting a realistic model before using any mathematical formulation. This method consists in recording TSC and TSL on a parametric $T(t)$ logarithmic X - Y display; we shall illustrate this proposition with the specific case of stannic oxide monocrystals.

Let us recall the functional equation set (1); for the sake

of present convenience in the discussion $[e\mu(T)E]$ will be considered as constant; special considerations will be given later when necessary to the case where $[e\mu(T)E]$ varies with temperature. $k/\tau_\lambda\{T(t)\}$ must be considered in a very general sense as a parameter relating the detected light [wavelength λ for the specific recombination center (RC)] and the recombining population $n_c\{T(t)\}$; the "lifetime" $\tau_\lambda\{T(t)\}$ is to be taken in a very broad sense including all situations from monoparticular (constant τ_λ) to biparticular (τ_λ proportional to the reciprocal RC density: $m^{-1}\{T(t)\}$).¹⁰ Equations (1) covers all the possibilities except for the case where the recombination process is not controlled by $n_c\{T(t)\}$ but by another mechanism (uncorrelated TSC-TSL).

In order to describe the correlative behavior of TSC and TSL on a logarithmic scale, let us first consider the classical "two-level" system of a single trap filling a recombination center (equal densities) through a conduction-band transfer:

$$\log J_{\text{TSC}} = \log(n_c\{T(t)\}) + \log(e\mu E) = Y,$$

$$\log J_{\text{TSL}} = \log(n_c\{T(t)\}) - \log\left(\frac{1}{k}\tau_\lambda\{T(t)\}\right) = X,$$

eliminating the functional $n_c\{T(t)\}$ which is rather difficult to calculate,¹⁴ it gives

$$Y = X + \log(\tau_\lambda\{T(t)\}) + \log(e\mu E/k). \quad (2)$$

At the very beginning of the thermally stimulated process, both TSC and TSL are faint enough so that quasiconstant populations of the levels are conserved; the system is considered as a reversible one and obviously τ_λ must be a constant. Then the asymptotic behavior of the parametric X - Y curve is necessarily a straight line of slope unity. If fractional emptying is employed (thermal cycling), the mobile point M must go back and forth on this line.

When TSP develops, the carrier density on the levels evolve in appreciable amounts; in the classical two-level system (Fig. 1) the TSL maximum (point A) must be reached first.¹¹ This corresponds in the X - Y plot to bending up the curve until the maximum (point B) of the TSC is reached. As soon as the curve deviates from the initial straight line, the system is nonreversible. If $e\mu E$ is allowed to vary, then the initial curve is not a straight line; the curvature depends on the $\mu(T)$ function and on the heating rate. The reversibility zone can then be determined only by thermal cycling experiments. At the high-temperature part of the peak, the process is obviously bimolecular, namely,

$$J_{\text{TSL}} = Kn_c\{T(t)\}m_\lambda\{T(t)\},$$

with the conservation law $m\{T(t)\} = n_c\{T(t)\} + n_t\{T(t)\}$. It can be asserted that $n_t\{T(t)\}$ goes to zero faster than $n_c\{T(t)\}$, then the condition $m\{T(t)\} = n_c\{T(t)\}$ can be taken as occurring asymptotically at the high-temperature range. This gives

$$J_{\text{TSL}} = Kn_c^2\{T(t)\},$$

$$\log J_{\text{TSL}} = 2 \log(n_c\{T(t)\}) + \log K = X,$$

$$\log J_{\text{TSC}} = \log(n_c\{T(t)\}) + \log(e\mu E) = Y,$$

$$Y = \frac{1}{2}X + \log(e\mu E/K^{1/2}).$$

The limiting curve is then a straight line of slope $\frac{1}{2}$; the gener-

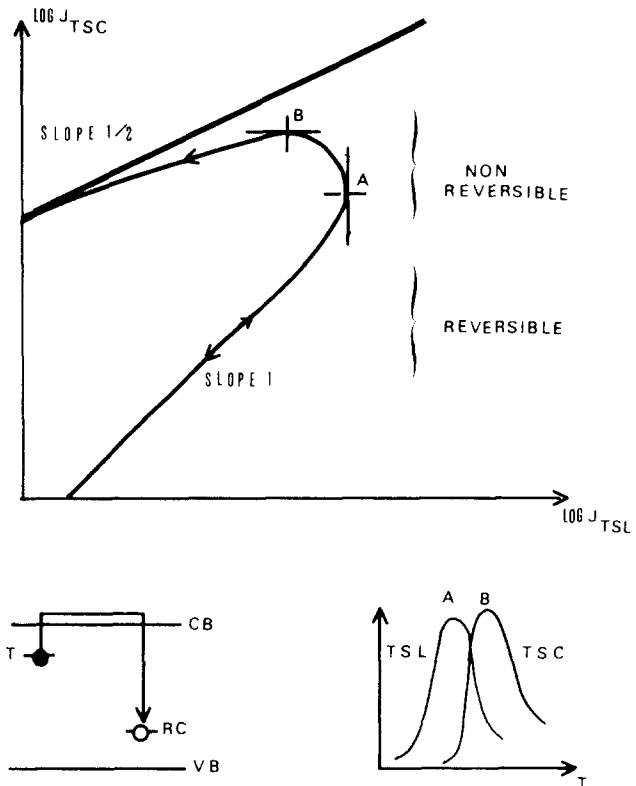


FIG. 1. Typical two-level behavior.

al behavior is sketched in Fig. 1.

Nevertheless, we must now take into account more complex situations arising from the simultaneous action of multiple kinds of traps or recombination centers. This method is intended to help clarify the situation.

Starting from a certain point M on the X - Y plot, one can use the direction of evolution as an indication of the leading mechanism. This is sketched on Fig. 2 (the temperature being kept rising). This leads to typical X - Y curves corresponding to typical situations. The most usual possibilities are assembled in Fig. 3 where deduced curves are reported. We should detail with a few words these depicted situations:

Case I. The successive and more or less overlapping

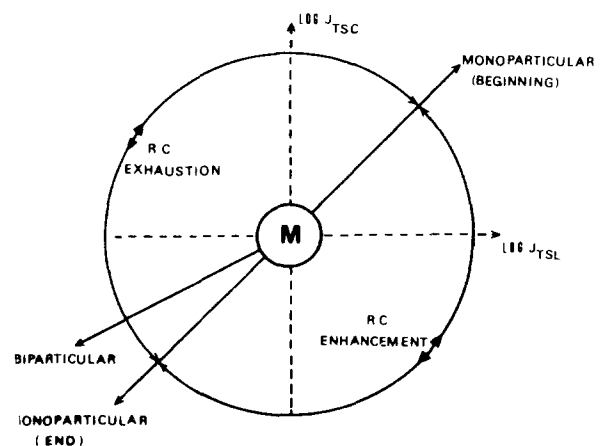


FIG. 2. Leading mechanism.

emission of electrons occurs from two distinct trap levels. They recombine on a single radiative recombination center.

Case II. Electrons from a single trap recombine into two distinct RC (one of them being radiatively detected). The fading of TSL is rather fast and should lead to a plateau. The final evolution (a) or (b) depends on the evolution of the lifetime of the conduction carriers. This effect is to be enhanced if, during TSL, the RC density is also reduced due to another process such as hole emission in the valence band.¹⁵

Case III. The RC density is strongly enhanced by an external mechanism (for instance ionic drift, sensitization or other). The exact shape of the curve depends on the time t where this process sets into action with respect to the TSC peak: (a) t is well before the maximum; (b) t is in the region of the maximum; (c) t is after the maximum.

An external case, extrapolated from case III, should be discussed independently and referred to as case IV; suppose that the holes are provided to the RC at a rate $\gamma \text{ cm}^{-3} \text{ s}^{-1}$, given by a mechanism distinct from the trap emission; suppose that the recombination is fast enough so that the rate of recombination (i.e., J_{TSL}) is kept equal to the rate γ , then the population $m_\lambda \{ T(t) \}$ on the RC adjusts automatically to keep these rates equal over a temperature range. This is a specific case of "uncorrelated" TSC and TSL, each of these phenomena belonging to two different origins. In this case Eqs. (1) are, of course, still valid but no *a priori* comment can be made on the evolution of m_λ (i.e., τ_λ).

J_{TSL} could be preferably written as $J_{\text{TSL}} = k' \gamma \{ T(t) \}$, if $\gamma \{ T(t) \}$ is the functional rate for supplying holes and k' a matching constant.

Then instead of Eqs. (1), we must consider the three-equation system (2)

$$\begin{aligned} J_{\text{TSC}} &= e\mu(T)En_c \{ T(t) \}, \\ J_{\text{TSL}} &= Kn_c \{ T(t) \} m \{ T(t) \}, \\ J_{\text{TSL}} &= k' \gamma \{ T(t) \}. \end{aligned} \quad (2)$$

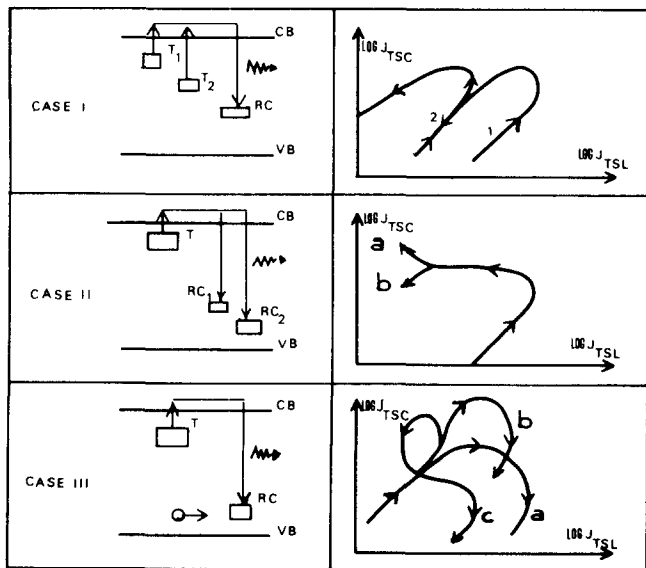


FIG. 3. Multiple center behavior (see text).

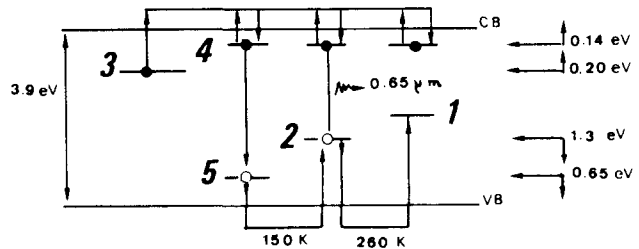


FIG. 4. Position of localized levels in SnO_2 band gap.

Then, expressing Eqs. (2) in its logarithmic X - Y form it is easily shown that $m \{ T(t) \}$ can be eliminated:

$$Y = X + \log(n_c \{ T(t) \}) - \log(\gamma \{ T(t) \}) + \log(e\mu E / k'). \quad (3)$$

In the most classical case where n_c and γ are activated variables (energies E_c and E_r):

$$\log n_c = \alpha \log \gamma, \quad \text{if } \alpha E_c / E_r,$$

then Eq. (3) gives a linear graph $Y = \alpha X$ very similar to a monoparticulate process except for the slope α that could differ from unity. This graph is eventually reversible.

As a general remark it must be remembered here that thermal cycling must be considered as a very good test to confirm the conclusions but is not needed in the operation itself.

Regarding a typical experimental situation where such complex kinetics may be examined, we have chosen stannic oxide monocrystal samples because some of us had investigated the traps¹²⁻¹⁴ with a complete set of dc and transitory experiments of photoconductivity and luminescence, leading to a precise knowledge of the behavior of trapped and recombining carriers. The global scheme of localized levels in the forbidden gap is represented in Fig. 4; for temperatures higher than liquid-nitrogen temperature it was shown that the main luminescent band related to RC_2 and this was also confirmed in thermoluminescence spectral analysis.^{12,13} The radiative transitions originate in the shallow traps 4 in thermal equilibrium with conduction band. Thermally excited carriers are electrons and their mobilities do not vary appreciably with temperature.

The main point essentially established from dc photoconductivity is that two mechanisms of continuous thermal quenching (CTQ) processes take place in the range of 130 and 260 K, respectively. The first CTQ consists in an emission of holes from RC_1 , and quickly recaptured by RC_2 , the second one is a similar thermally assisted transfer of holes from RC_2 to RC_1 .

During these processes the contribution of holes to the electrical conductivity is to be neglected but the variations in the electron lifetime in conduction band is important.

We show in Fig. 5 a typical record of both TSC and TSL obtained on stannic oxide monocrystals grown from vapor phase by de Murcia.¹⁶ It is to be noted that two peaks are clearly seen in TSL, whereas TSC is not so selective: it has also been found that, despite a general similarity in the shapes, the activation energies of the low temperature part of

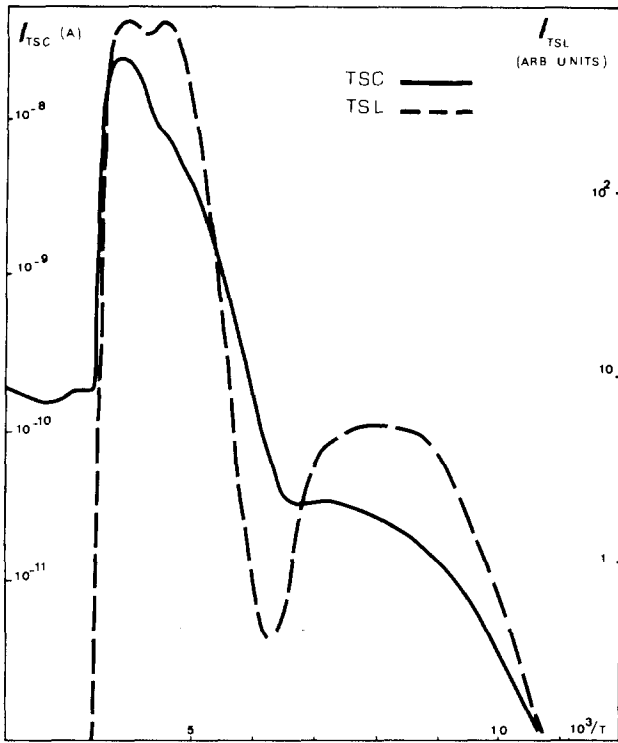


FIG. 5. Simultaneous TSC and TSL in SnO_2 monocrystals after uv excitation ($\beta = 0.5 \text{ ks}^{-1}$).

the peaks differ considerably.

More detailed conclusions can be presented if we look at a correlative X - Y plot of $\log(\text{TSC})$ and $\log(\text{TSL})$ (Fig. 6). On the same graph we also reported thermal cyclings in order to determine the reversible regions. It clearly appears that the recombination mechanisms involved in the low- and high-temperature range belong to completely different ki-

netics despite the fact that the emitted light is of the same spectra composition. The low-temperature peak can be entirely wiped out by fractional emptying without altering the high-temperature peak. The first low-temperature rise is monoparticular and reversible; the plateau shows that the recombination centers are quickly filled without affecting n_c .

The high-temperature peak takes place on the same RC_2 transition with a mechanism triggered by temperature ($T > 160 \text{ K}$ corresponding to the first CTQ). The behavior is similar to a monomolecular process except the slope $\approx \frac{1}{2}$ of the line; the exhaustion occurs with a stabilisation of τ_λ (i.e., m_λ) of fractional emptying is performed; this means that RC_2 is not the true reservoir for holes. These conclusions are in good agreement with case IV of a recombination regulated by the holes coming into RC_2 . This is also in accordance with the observed CTQ mechanism transferring holes from RC_3 to RC_2 .

The slope $\frac{1}{2}$ is roughly in agreement with the ratio of activation energies 0.34 and 0.65 eV respectively found for populations n_c and m_s .

As a conclusion it can be said that the correlative behavior of TSC and TSL, as it appears on a logarithmic X - Y plot, could be of some help in identifying the mechanism of carrier exchange that motivates the TSP. This qualitative knowledge is needed before developing any mathematical solution of the thermally stimulated process. The parametric form of the curve depends rather critically on the typical situation involved in the relaxation; the conclusions can also be supported by fractional emptying but these experiments are not required systematically. In the particular case of a SnO_2 monocrystal where a complicated transfer was independently proven to occur, it was shown that the various mechanisms are satisfactorily confirmed on the X - Y graph. This leads to the idea that the technique could be used directly as a

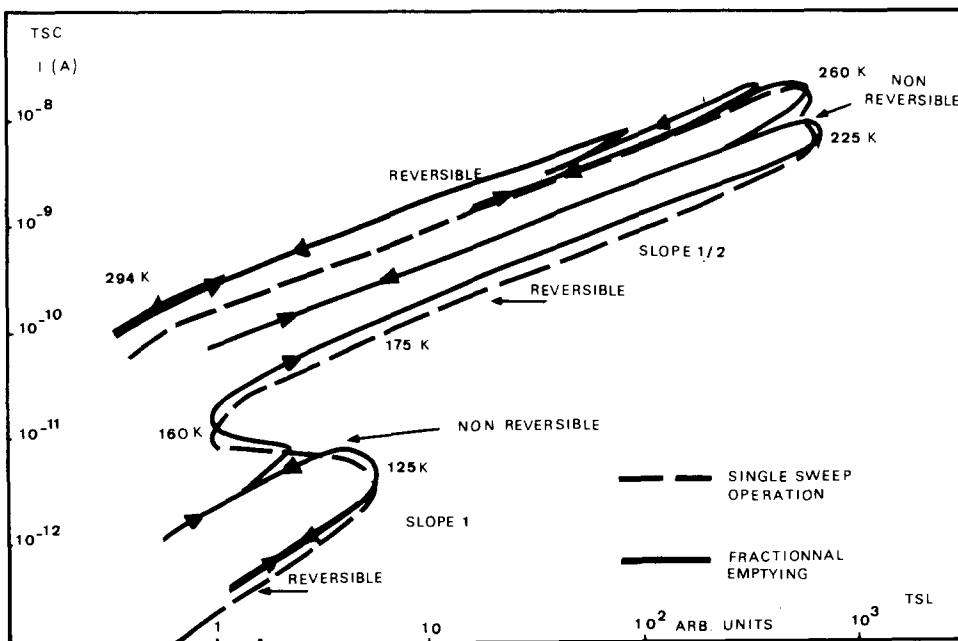


FIG. 6. Parametric TSL TSC plot for stannic oxide monocrystal.

characterization tool of less-known material if TSC and TSL are simultaneously available, even at a low level.

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