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Deconvolution of the transient photocurrent signals: application to the study of the density of states of a BTO crystal

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Abstract
The density of states of a lead doped sillenite crystal $Bi_{12}TiO_{20}$ (BTO:Pb) was investigated by means of the modulated photocurrent (MPC) and transient photocurrent (TPC) techniques. The modulated photocurrent signal as well as the TPC transients are limited by the bandwidth of the measurement systems. The MPC signal can be easily corrected by the measurement of the phase shift and modulus modification introduced by the measurement system. We propose a method to correct the TPC transient limitation and illustrate it by means of a simulation. Further, this method is applied to experimental data and we compare the density of states extracted from both methods applied to the same BTO:Pb crystal.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Characterization of the density of electrically active defects in semiconductors helps to refine the growth or deposition conditions of these materials to eventually obtain the properties required for a given application. Because of the high resistivity of semi-insulating materials the characterization techniques are rather few and mostly based on photoconductive properties. Among all these techniques the modulated photocurrent (MPC) and the transient photocurrent (TPC) techniques are two techniques that should lead to the same spectroscopy, since it has been demonstrated that the MPC technique is simply the Fourier transform of the TPC experiment [1]. In both techniques one face of the sample is fitted with parallel electrodes 1–2 mm apart and a dc bias is applied to them. In the MPC experiment [2–4] the sample is illuminated by a flux of light modulated at an angular frequency ω whose photon energy is larger than the band gap of the material. The modulus and the phase shift ϕ referred to the excitation of the resulting ac photocurrent are measured and a density of states (DOS) spectroscopy is achieved from these quantities measured at different frequencies and temperatures. It is possible to correct ϕ from the measurement system response itself by recording the phase shift ϕ_{cor} induced by the system with a fast photodiode. This correction is never perfect since it depends on the time response τ_r of the fast photodiode itself. However, considering the maximum pulsation ω_{max} used in the MPC experiment, in most cases $1/\tau_r \gg \omega_{max}$, which is sufficient to allow extraction of the DOS considering a global phase shift equal to $\phi_g = \phi - \phi_{cor}$. In the TPC experiment one is also faced with the same limitations as in MPC: the response time or the limited bandwidth of the measurement system. When this bandwidth is small, a proper DOS spectroscopy requires the measurement of the transient photocurrent at many temperatures, say every 20 K or even every 10 K. The temperature step in between any two such temperatures can be increased in accordance with available bandwidth.

In this paper we show that it is possible to 'artificially' extend the bandwidth of a measuring system in the TPC experiment. This is first shown on a theoretical basis and by means of numerical simulations. This method is further applied to the study of a Pb doped crystal of $Bi_{12}TiO_{20}$ (BTO:Pb) and the results of the TPC experiment are compared to those of an MPC experiment applied to the same sample.

2. Experimental details

The BTO:Pb crystal was grown in Brazil [5]. It was fitted with two aluminium strips 2 mm apart biased with 100 V. The band gap of this material is of the order of 3.1–3.2 eV, so band to band generation requires photon energies larger than this value, that is, wavelength smaller than 390 nm.

In the MPC experiment the flux of light was provided from a set of light emitting diodes ($\lambda = 385$ nm). This light was modulated from $f = 12$ Hz to 40 kHz in a geometrical progression ($f_{i+1} = 1.5 \times f_i$). The temperature was varied from 100 to 460 K in 10 K steps. The variations of the phase shift ϕ and modulus of the ac photocurrent $|I_{ac}|$ with temperature and frequency were recorded with a lock-in amplifier. After correction of the phase shift, a DOS spectroscopy can be achieved by means of different sets of equations.

A first method was proposed by Brüggemann *et al* that gives [3]

$$\frac{NC}{\mu} = \frac{2}{\pi}\left[\frac{Sq\xi G_{ac}\sin(\phi_g)}{|I_{ac}|} - \frac{\omega}{\mu}\right], \tag{1}$$

an equation in which the last term (ω/μ) is usually negligible. A second method was proposed by Hattori *et al*, giving [6]

$$\frac{NC}{\mu} = Sq\xi G_{ac}\omega\frac{\mathrm{d}}{\mathrm{d}\omega}\left[\frac{\cos(\phi_g)}{|I_{ac}|}\right]. \tag{2}$$

In these equations N is the density of states, C is the electron capture coefficient of the states, μ is the carrier mobility, ξ the applied field, q the absolute charge of the electron, G_{ac} the ac generation rate and S the conduction cross-section through which the current is flowing. Note that the quantity NC/μ depends only on these known parameters and in the following it is this quantity, called reduced DOS or r-DOS, that we shall try to extract from the results of the experiments. It must be underlined that the second method (Hattori's method) leads to sharper definition of the r-DOS, revealing more clearly the presence of peaks, if they exist, than the first one (Bruggemann's method), but it has the main drawback that it depends on a derivative and often leads to more noisy DOS than the Bruggemann's method if the experimental data are noisy.

If one assumes that the electrons are the majority carriers in both methods, the energy scaling is achieved according to

$$E_c - E = k_b T \ln(CN_c/\omega), \tag{3}$$

in which k_b is the Boltzmann constant and N_c the equivalent density of states at the bottom of the conduction band.

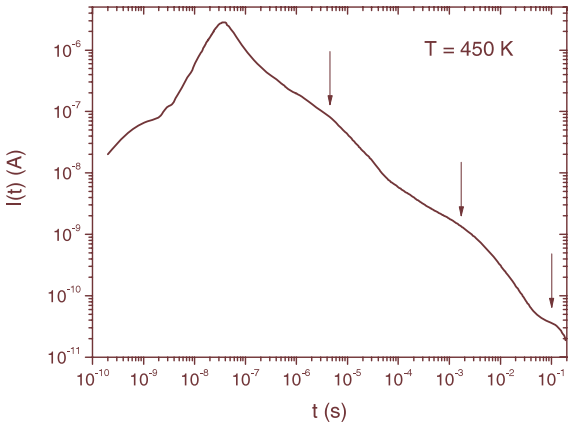

Figure 1. Variations with time of a transient photocurrent recorded at 450 K.

The quantity CN_c, often referred to as an attempt-to-escape frequency ν, is usually unknown. Since the purpose of this paper is to compare the results of two techniques (MPC and TPC) applied to the same sample, we do not need the exact value of ν and will use the same approximate value of 10^{12} s^{-1}.

In the TPC experiment the excitation light consisted of a pulse (3 ns) from a nitrogen laser (337 nm). The variations of the current were recorded from the voltage drop in a resistor in series with the crystal. This voltage drop was amplified with a 10 MHz bandwidth amplifier and recorded on a 125 MHz oscilloscope. Different time scales were chosen on this oscilloscope to record the transient current variations from 10 ns to 0.2 s. At short times the resistor value was 100 Ω and this value was progressively increased to 1 MΩ at very long time so as to improve the sensitivity. The transient photocurrents were recorded from 100 to 450 K at 50 K intervals. The injected charge in the crystal, i.e. the generation rate, was estimated from the response of a calibrated fast photodiode.

Main has shown that from a Fourier transform applied to the transient photocurrent it was possible to deduce the r-DOS of the material applying the same equations (1)–(3) to the phase and modulus deduced from this Fourier transform [1]. Therefore, one should obtain the same r-DOS with each technique if applied to the same materials.

We present in figure 1 the variation versus time of the transient current at a temperature of 450 K. Arrows on the figure identify structures that are certainly linked to the emission of carriers from traps of the crystal. Due to the limited bandwidth of the amplifier, it is clear that the transient current evolution at short times, say in between 10 ns and 0.1 μs, is altered by the measurement system response time. This is why we have investigated the possibility of improving the data recording and r-DOS deduction from TPC taking account of the system response time.

3. Numerical simulations

It is well known in signal treatment that during a measurement the recorded global response $I(t)$ is the convolution product

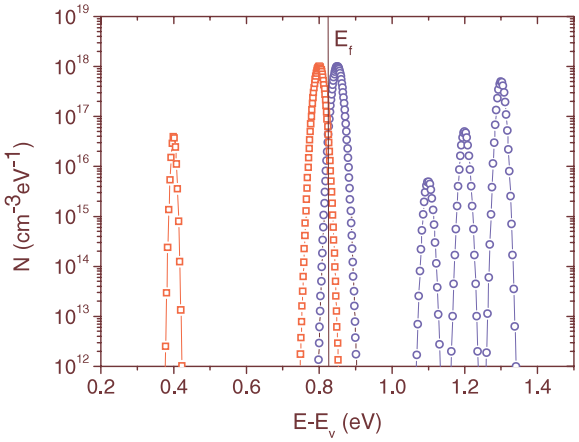

Figure 2. DOS used in the simulations.

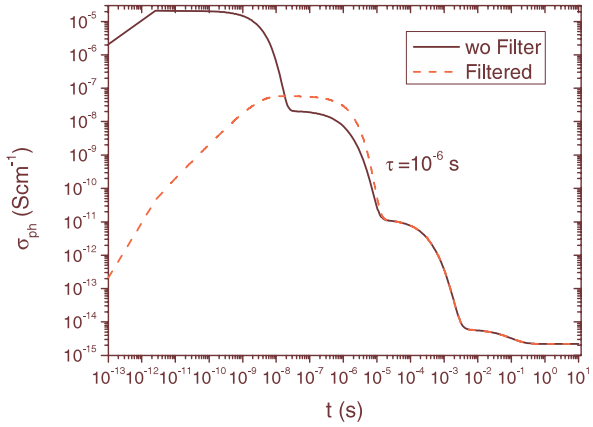

Figure 3. Transient photoconductivity with (Filtered) and without (wo Filter) first order filtering.

between the 'true' signal $S(t)$ and the system response $R(t)$: $I(t) = S(t) \otimes R(t)$. However, in the frequency domain, after a Fourier transform of the global response, this convolution product transforms into a simple product and therefore it is theoretically possible to extract the 'true' signal provided the system response is known.

To demonstrate that this deconvolution technique is applicable to TPC transients, we have performed numerical simulations of this experiment. In these simulations one can choose a DOS distribution and the continuity equations are solved by means of an Euler implicit method. We present in figure 2 the DOS distribution we have studied.

The virtual semiconductor we considered has a gap of 1.5 eV. The equivalent densities of states at the bottom of the conduction band and at the top of the valence band were both taken equal to 2.5×10^{19} cm^{-3} at 300 K. The Fermi level is pinned above the middle of the gap ($E_f - E_v = 0.825$ eV) by two peaks of states: one donor peak ($N_{max} = 10^{18}$ cm^{-3} eV^{-1}, $E_{max} - E_v = 0.65$ eV and a standard deviation $\sigma = 10$ meV, open squares) and an acceptor peak ($N_{max} = 10^{18}$ cm^{-3} eV^{-1}, $E_{max} - E_v = 0.70$ eV, $\sigma = 10$ meV, open circles). Three peaks of acceptor states (open circles) are located in the upper part of the gap ($N_{max} = 5 \times 10^{17}$ cm^{-3} eV^{-1}, $E_{max} - E_v = 1.3$ eV; $N_{max} = 5 \times 10^{16}$ cm^{-3} eV^{-1}, $E_{max} - E_v = 1.2$ eV; $N_{max} = 5 \times 10^{15}$ cm^{-3} eV^{-1}, $E_{max} - E_v = 1.1$ eV, with the same standard deviation $\sigma = 8$ meV) and a single peak of donor states (open squares) is set at $E_{max} - E_v = 0.4$ eV with a maximum $N_{max} = 4 \times 10^{16}$ cm^{-3} eV^{-1} and $\sigma = 5$ meV. Since it is not our purpose here to study the influence of different capture coefficients for each states, the capture coefficients for holes and electrons were taken identical for all the states, $C = 10^{-8}$ cm^3 s^{-1}. The electron and hole extended state mobilities were chosen equal to $\mu_n = 100$ cm^2 V^{-1} s^{-1} and $\mu_p = 0.1$ cm^2 V^{-1} s^{-1} respectively so that the recorded transients are definitely linked to the electron behaviour. The number of increments along the energy axis was taken equal to 500. The filtering of the signal was done assuming a first order filter with time constant τ and numerically solving the classical equation

$$V_{out} + \tau \frac{dV_{out}}{dt} = V_{in} \quad (4)$$

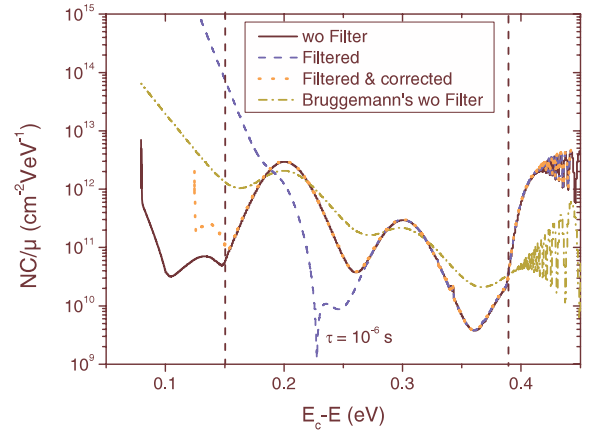

Figure 4. r-DOS extracted by means of Hattori's method from the transients of figure 3 calculated with filter (dashed line) or without filter (full line). The r-DOS calculated with a filter but corrected (dotted line) is also shown. The r-DOS calculated from the unfiltered transient by means of Bruggemann's method is displayed with a dash–dotted line.

where V_{out} is the signal out of the filter and V_{in} the signal entering the filter.

We show in figure 3 the influence of such a filter, in which $\tau = 10^{-6}$ s, on the transient photoconductivity signal σ_{ph} calculated for a temperature of 200 K.

Clearly, after filtering, one of the bumps, the signature of the existence of a defect peak, is drowned in the global response limited by the bandwidth and the information concerning this defect may be lost. This is obviously reflected in the r-DOS determination as shown in figure 4. The r-DOS has been extracted from the Fourier transform of the different transients calculated by the simulation. For the unfiltered transient both methods presented in the previous section have been used for this purpose. Considering the temperature at which the simulation was performed (200 K) only the two defect peaks close to the conduction band have an influence on the calculated transient and thus can be probed. It can be seen, as we mentioned in a previous section, that the Hattori's method gives a better resolution of the peaks that are

well defined and well separated. However, the Bruggemann's method also reveals both peaks though they appear wider.

As far as filtering is concerned it appears, as could be predicted by the drowning of one bump of the transient current into the global response of the system, that the upper peak is not well reproduced to say the least and a spike is clearly seen that has no link with the probed DOS.

The filtering can be corrected by taking into account of the phase shift and modulus evolution introduced by the filter itself. For the same ω values we used to calculate the Fourier transform of the signal, the phase shift and modulus modification have been calculated from the well known analytical expressions coming from the Fourier transform of equation (4) and the Fourier transform values of the filtered transient have been corrected accordingly. It can be seen that this correction is rather efficient since the shallowest peak is revealed as it is with the unfiltered transient. Hence it should be theoretically possible to extend the bandwidth of the measurement system taking into account its response time.

We would like to underline that all this procedure requires numerical treatment. The Fourier 'transforms' are numerically calculated over a limited time range (the time range of the signal) and with a discrete signal (our signal is made of a succession of points). This certainly introduces errors in the Fourier calculation, and this is why we have added two vertical dashed lines in figure 4. Outside these lines the r-DOS we calculate has nothing in common with the proper DOS, the curves obtained being essentially linked to the calculus errors and limitations.

This behaviour can be illustrated by the DOS behaviour at high energies, i.e. low frequencies. For energies higher than the limit fixed by the vertical dashed line one observes a sudden rise of the 'DOS' followed at very deep energies by some fringes. This behaviour is simply linked to the limited time range under which the simulation has been performed. The Fourier transform should be calculated for $-\infty < t < +\infty$ but our calculation extended only to 10 s. Hence the Fourier transform is calculated for (the signal) $\times$ (a rectangular window equal to 1 from 0 to 10 s and null outside this time interval). It is this rectangular window that is responsible for the observed fringes at deep energies, the Fourier transform of a rectangular window giving a function $\sin(x)/x$ that gives rise to this fringed 'DOS'. It must be underlined that these fringes are seen if one calculates the Fourier transform, and hence the r-DOS, with very low ω. For the data shown in figure 4 the lowest ω was taken equal to unity. Experimentally, this characteristic part of the curve can be easily removed either by rejecting the calculated 'DOS' or by limiting the range of ω used in the Fourier transform calculation.

Concerning the part of the r-DOS at shallow energies we believe that we are faced with the same problem: when the contribution to the Fourier transform of the rectangular window predominates over the contribution of the signal, the r-DOS has only a little connection with the true r-DOS. Unfortunately, there is no easy means to determine at which energy, or which ω, the behaviour happens. This problem is even more acute experimentally, since we ignore the exact shape of the DOS. However, we shall propose in the next section a method to determine the r-DOS shape.

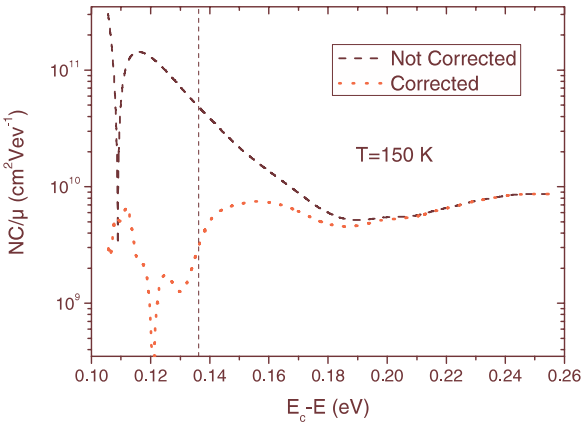

Figure 5. r-DOS deduced from transient recorded at 150 K corrected (dotted line) and not corrected (dashed line) for the system response.

4. The BTO:Pb density of states

Experimentally, to determine the response time of the apparatus we have replaced the sample by a fast photodiode and recorded a transient current with this fast photodiode. The Fourier transform of this transient was calculated as we did with the experimental transients obtained with the BTO:Pb crystal (the same range of ω and same ω values). The phase shift and modulus of the Fourier transform of the currents recorded with the BTO:Pb crystal were corrected according to the phase shift and modulus calculated from the fast photodiode response. From these corrected data we deduced the r-DOS of the BTO:Pb crystal at different temperatures.

We present in figure 5 the r-DOS deduced from the transient photocurrent recorded at 150 K by means of the Bruggemann's method. Actually both methods, Hattori's and Bruggemann's, were used, but because of the derivative involved in the Hattori's method the r-DOSs were rather noisy.

It can be seen in figure 5 that the r-DOS corrected for the system response exhibits a bump that was completely invisible in the uncorrected r-DOS. The lowest ω used in the Fourier transform was taken equal to 1000 rad s^{-1} and we avoided the problem found at deep energy in the theoretical section. For energies above the dashed line we have estimated that the calculation was not reliable, and this part of the curves was systematically suppressed from the r-DOS curves obtained at different temperatures. This suppression was done after superimposition of the r-DOS curves obtained at different temperatures.

With the correction for the system response we could put together the r-DOS curves obtained each 50 K from 100 to 450 K. The total r-DOS is displayed in figure 6, where it can be compared with the r-DOS deduced from the MPC measurements. The global shape is the same, though some peaks seem much higher as measured from TPC compared to those found with MPC. Vertical lines underline this correspondence. Even a small peak, indicated by an arrow, appears around 0.38 eV, that was almost unseen with the MPC technique. However, the peaks located at ~0.16, ~0.32 and ~0.77 eV seem to have the same relative amplitudes in both techniques.

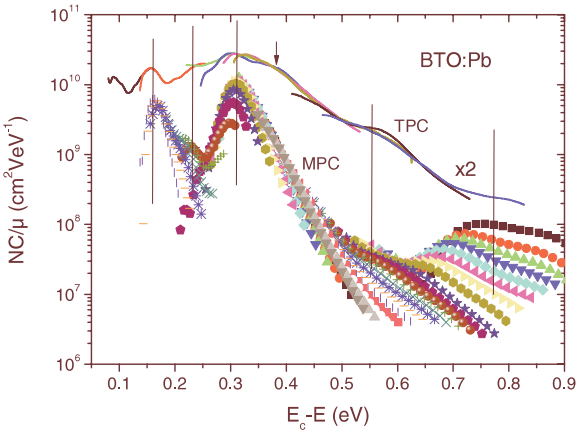

Figure 6. Comparison of the r-DOS obtained on the same crystal of BTO:Pb by means of the TPC and MPC technique. The TPC curve has been multiplied by two to give a clear picture.

This result is quite surprising, since we were expecting to extract the same r-DOS by both techniques. The main difference in each experiment is the wavelength of the light used to probe the material. Practically, it was impossible to find light sources with the same wavelength for both experiments. In the MPC technique we used a set of nine light emitting diodes, for their ease of being driven by a modulated bias, at $\lambda = 385$ nm (3.22 eV) and in the TPC experiment we used a pulsed nitrogen laser emitting at $\lambda = 337$ nm (3.68 eV). We propose that the probed volume of the crystal is different from one technique to the other. Because of the lower photon energy, close to the bandgap width, the MPC technique is probably probing the defect states deeper in the crystal, i.e. farther from the surface, than the TPC method, because of the expected differences in the absorption coefficients for the two wavelengths we used. Besides, it was shown that the MPC technique was always measuring the lowest NC/μ [4]. Hence, if some defect densities are decreasing from the surface toward the bulk, as it could be expected, it is not surprising to find a lower r-DOS for some of them with the MPC than with the TPC experiment: the MPC results will reflect the lower NC/μ in the probed volume.

Finally, we also want to underline that the peak indicated by an arrow was detected from a time of flight experiment performed on the same crystal with the same wavelength as we used for the TPC [7].

5. Conclusion

We have shown that it was theoretically possible to extend artificially the bandwidth of the measurement set-up used for TPC experiment. Taking advantage of the fact that the density of states probed by this technique is revealed by means of a Fourier transform of the transient current, the bandwidth limitation of the system can be overcome to a significant and useful extent by a deconvolution of the signal. Numerical simulations of the TPC experiment demonstrate that, once the transient is corrected from some filtering influence, it is possible to recover the complete DOS spectrum as if the measurement system were quasi-perfect.

Experimentally, the response time of the system was measured by means of a fast photodiode and it is clear that the deconvolution of the transient signal extends the energy range of the probed DOS at a given temperature. Thus, with such a procedure one can increase the temperature difference between two recordings. In the present case the DOS was probed varying the temperature from 100 to 450 K in 50 K steps.

After correction, the r-DOS we obtained from the TPC data was compared to the r-DOS measured on the same crystal by means of the MPC technique. The peak positions were found to be the same but the maxima of some of them were found to be higher when probed by the TPC technique than when probed by the MPC experiment. We suggest that these differences can be attributed to the different wavelengths used in each technique. The peaks found to be higher in the TPC technique than in the MPC can probably be attributed to surface states since the TPC experiment was performed with a light absorbed in a region closer to the surface than the MPC technique.

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