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Fourier-transform analysis of multiexponential curves observed in photoconductivity studies

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A method is proposed to analyze multiexponential and delayed components in the relaxation curves observed in photoconductivity processes. The amplitudes, time constants, and delayed time (escape time from the traps) have been determined from the real or imaginary parts of the fast Fourier transform of the recorded data. This technique permits us to analyze uniquely the complete form of the transient response without ambiguity, in contrast to numerical, graphical, or curve-fitting approaches. The above method has general applicability in other fields dealing with multiexponential transient phenomena. On this basis, a commercially available CdS photodetector was examined and time constants were determined precisely. The obtained values are in close agreement with earlier reported values from other techniques.

I. INTRODUCTION

It is well known[1–3] that transient photoconductivity provides, in principle, information about trapping centers, recombination processes, and transport behavior of free charge carriers.

Even though the basic mechanisms are clear, the analysis of the relaxation curves is rarely successful on getting significant information of the traps parameters. This is because there are fundamental impediments in analyzing these curves uniquely and precisely. Nonequilibrium processes in photoconductors are approximately described by a hard-to-solve (or improbable to solve) set of nonlinear differential equations. Naturally, a comparative study of experimental and theoretical results are out of the question.

The kinetics of the charge carriers in photoconductors under nonequilibrium conditions is really a complex issue and the trend of the relaxation process cannot be generalized. One of the reasons for this is a recombination process which can be linear, quadratic, a combination of both, or even proportional to the third or odd power of an excess of charge carriers. Linear recombination is very common for intermediate intensities (10^{10} photons/cm^2 s $< I < 10^{18}$ photons/cm^2 s), and for very high and very low intensities the relaxation curve deviates from the exponential nature. In the former case, the recombination process becomes quadratic and in the later case, photomemory or persistent photoconductivity is predominant. In conventional semiconductors, such as II-VI and III-V compounds, linear recombination process is more common for a wide range of intensities.

In the presence of trap-dominated photoconductors, the situation is slightly different. For the linear recombination case, the solution of the set of nonlinear differential equations is given as the sum of the exponential terms. Obviously, in phenomenological models the use of the sum of exponential terms is also frequent.[4,5] When the above requirements are met, then the rise and decay curves are expressed by

$$I_{\mathrm{ph}}(t)=\begin{cases}\sum_{i=1}^{M} I_i(1-e^{-\alpha_i t}), & \text{rise} \quad (1a)\\ \sum_{i=1}^{M} I_i e^{-\alpha_i t}, & \text{decay} \quad (1b)\end{cases}$$

where I_{ph} is the photocurrent and $\alpha_i \equiv 1/\tau_i$ is the time constant for a particular process. I_i is the contribution from the ith process. Summation goes up to M, where M is the number of contributing components.

If the recombination process is other than linear or the time constant varies during the process, then the form of the relaxation curve is far different than that of the exponential curve and different techniques should be used.

The analysis of Eqs. (1a) and (1b) when dealing with multiexponential terms, is itself a crucial and a challenging problem. An analytical method does not exist and those normally used are notoriously unreliable.[6] When there are more than two terms, then, the analysis of the curve and meaningful information from it becomes a big issue. The situation is further complicated when the delayed contribution from the traps in the photocurrent is significant and a reliable approach does not exist to analyze such curves.

Multiexponential curves appear not only in photoconductivity but also in physical, chemical, and biological sciences. The purpose of the present paper, therefore, is to propose a new approach to examine multicomponent exponential signals that will have a general applicability.

II. FOURIER-TRANSFORM APPROACH FOR ANALYZING MULTICOMPONENT AND DELAYED CONTRIBUTIONS

It is a well-known property of Fourier transformation that a time delay is converted into a phase shift in the frequency domain, i.e., the Fourier transform is multiplied by $\exp(-i\omega\tau_0)$.[7,8] This means that real and imaginary components of a Fourier transform show oscillations. By exploiting this aspect, delayed components have been detected and their contributions were estimated separately.

The above method can be generalized by

$$I_{\mathrm{ph}}(t)=\begin{cases}\displaystyle\sum_{i=1}^{M} I_i(1-e^{-t/\tau_i})+u(\lambda)\sum_{j=1}^{K} I_j[1-e^{-(t-\tau_{0j})/\tau_j}], & \text{rise} \qquad (2a)\\ \displaystyle\sum_{i=1}^{M} I_i e^{-t/\tau_i}+u(\lambda)\sum_{j=1}^{K} I_j e^{-(t-\tau_{0j})/\tau_j}, & \text{decay} \qquad (2b)\end{cases}$$

where $u(\lambda)$ is a step function and is defined as

$$u(\lambda)=0 \quad \text{for } t<\tau_{0j}\ ,$$

$$u(\lambda)=1 \quad \text{for } t>\tau_{0j}\ .$$

Here, the summation for delayed terms goes from 1 to K, where K is the number of types of traps which hold charge carriers for a certain time, thus, contributing in a delayed signal.

The real and imaginary parts of the Fourier transform of Eqs. (2) are given by

$$\begin{aligned}\mathrm{Re}(\omega)&=\sum_{i=1}^{M} I_i\delta(0)+\sum_{j=1}^{K} I_j\delta(0)-\sum_{i=1}^{M}\frac{I_i\alpha_i}{\alpha_i^2+\omega^2}\\ &\quad-\sum_{j=1}^{K}\frac{I_j\alpha_j\cos(\omega\tau_{0j})}{\alpha_j^2+\omega^2}+\sum_{j=1}^{K}\frac{I_j\omega\sin(\omega\tau_{0j})}{\alpha_j^2+\omega^2}\ ,\\ \mathrm{Im}(\omega)&=\sum_{i=1}^{M}\frac{\omega I_i}{\alpha_i^2+\omega^2}+\sum_{j=1}^{K}\frac{I_j\omega\cos(\omega\tau_{0j})}{\alpha_j^2+\omega^2}\\ &\quad+\sum_{j=1}^{K}\frac{I_j\alpha_j\sin(\omega\tau_{0j})}{\alpha_j^2+\omega^2}\end{aligned} \qquad (3a)$$

$$\begin{aligned}\mathrm{Re}(\omega)&=\sum_{i=1}^{M}\frac{I_i\alpha_i}{\alpha_i^2+\omega^2}+\sum_{j=1}^{K}\frac{I_j\alpha_j\cos(\omega\tau_{0j})}{\alpha_j^2+\omega^2}\\ &\quad-\sum_{j=1}^{K}\frac{I_j\omega\sin(\omega\tau_{0j})}{\alpha_j^2+\omega^2}\ ,\\ \mathrm{Im}(\omega)&=-\sum_{i=1}^{M}\frac{I_i\omega}{\alpha_i^2+\omega^2}-\sum_{j=1}^{K}\frac{I_j\alpha_j\cos(\omega\tau_{0j})}{\alpha_j^2+\omega^2}\\ &\quad-\sum_{j=1}^{K}\frac{I_j\alpha_j\sin(\omega\tau_{0j})}{\alpha_j^2+\omega^2}\ .\end{aligned} \qquad (3b)$$

In addition to the above set, a separate equation can be constructed by equating the total value of the saturated photocurrent to the sum of all the components. Accordingly,

$$I_{\mathrm{ph}_{ss}}=\sum_{i=1}^{M} I_i+\sum_{j=1}^{K} I_j, \quad \text{rise} \qquad (4a)$$

$$I_{\mathrm{ph}}(0)=\sum_{i=1}^{M} I_i, \quad \text{decay} \qquad (4b)$$

where, $I_{\mathrm{ph}_{ss}}$ is the saturated value of photocurrent and I_{ph} is the initial value. The values of the frequency $w_n(w=2\pi n/N$, where N is the number of data points used), the real and imaginary parts of the Fourier transform and saturated values of the photocurrent (precisely obtained from the recorded signal) are all known quantities. Therefore, it can be seen that the system of Eqs. (3a) and (3b) together with Eqs. (4a) and (4b) provides sufficient and necessary information in order to obtain the values of I_i, I_j, τ_i, τ_j, and τ_{0j} uniquely and precisely.

III. EXPERIMENTAL PROCEDURE

In order to verify the validity of the above procedure, the experiment was performed on a commercially available CdS photodetector, purchased at Clairex Electronics Company (model 602). The detector was radiated with a wavelength of 515 nm, where the response is nearly maximum. The light intensities ranged from 10^{10} to 10^{13} photons/cm^2 s. The transient form of the rise and decay curves was obtained with the usual method and recorded by a signal averager PAR model 4203, in a digitized form and transferred to an IBM PC/XT computer through an RS 232C serial data interface. The obtained rise curve is shown in Fig. 1(a).

The Fourier transform of the obtained data was performed with the help of a conventional Cooley-Tukey algorithm. It was found convenient to process 2^9 data points for this purpose. The real and imaginary parts of the Fourier transform were obtained and a typical one is shown in Fig. 2. From the obtained peak it is clear that there exists a delayed term. With the help of Eqs. (3a) with (4a) (for rise curve) or Eq. (3b) with (4b) (for decay curve), a set of simultaneous equations was constructed. These sets of equations were solved for I_i, I_j, τ_i, τ_j, and τ_{0j} by a suitable method or with a proper program. Using these values, the relaxation curves were constructed and compared.

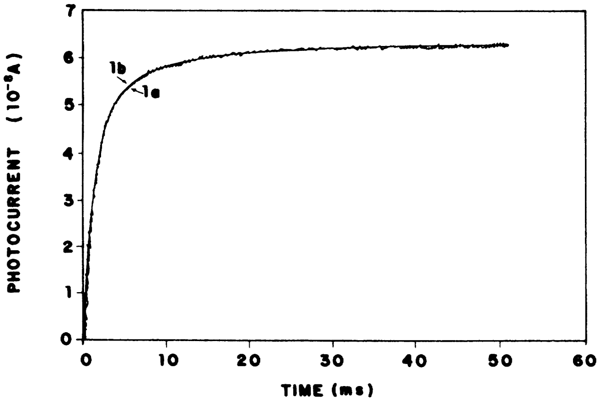

FIG. 1. Relaxation form of photoconductivity rise curves. (a) An experimental recorded curve. (b) A curve simulated with the help of Eq. (7).

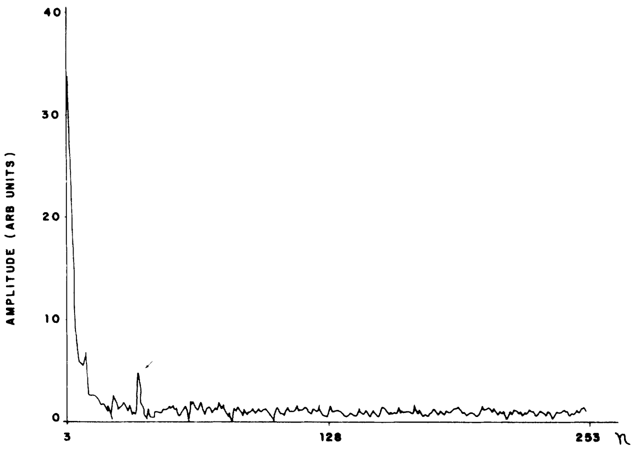

FIG. 2. Real part of the fast Fourier transform obtained from the recorded data. A genuine peak, marked by an arrow, shows the presence of a delayed component.

IV. RESULTS

Time-dependent behavior of photocurrent becomes

$$I_{\mathrm{ph}}(t)=I_1(1-e^{-t/\tau_1})+I_2(1-e^{-t/\tau_2})$$
$$+u(\lambda)I_3[1-e^{-(t-\tau_0)/\tau_3}] \,. \tag{5}$$

Here, we have assumed that the significant contribution comes from only two types of traps (see discussion).

For a time $t<\tau_0$, the delayed term has no effect on the very first equations of 3(a), since I_j, the contribution of the traps, is equal to zero. Thus, the first four equations are greatly simplified and they reduce to a system with no delay. With Eq. (4a), the remaining two equations to complete the set of seven equations are constructed as in Eq. (3a).

The set of Eqs. (3a) and (4a) in the present case (two trapping centers: one delayed and the other an instantaneous recombination center) is converted into the following equations:

$$I_{\mathrm{ph}_{ss}}=I_1+I_2+I_3 \,, \tag{6a}$$

$$\mathrm{Re}(0)=I_{\mathrm{ph}_{ss}}-\frac{I_1}{\alpha_1}-\frac{I_2}{\alpha_2} \,, \tag{6b}$$

$$\mathrm{Re}(\omega_1)=-\frac{I_1\alpha_1}{\alpha_1^2+\omega_1^2}-\frac{I_2\alpha_2}{\alpha_2^2+\omega_1^2} \,, \tag{6c}$$

$$\cdots \,, \tag{6d}$$

$$\mathrm{Re}(\omega_3)=\cdots \tag{6e}$$

$$\mathrm{Re}(\omega_{p_1})=-\frac{I_1\alpha_1}{\alpha_1^2+\omega_{p_1}^2}-\frac{I_2\alpha_2}{\alpha_2^2+\omega_{p_1}^2}-\frac{I_3\alpha_3\cos(\omega_{p_1}\tau_0)}{\alpha_3^2+\omega_{p_1^2}}$$
$$+\frac{I_3\omega_{p_1}\sin(\omega_{p_1}\tau_0)}{\alpha_3^2+\omega_{p_1^2}} \,, \tag{6f}$$

$$\mathrm{Re}(\omega_{p_2})=-\frac{I_1\alpha_1}{\alpha_1^2+\omega_{p_2}^2}-\frac{I_2\alpha_2}{\alpha_2^2+\omega_{p_2}^2}-\frac{I_3\alpha_3\cos(\omega_{p_2}\tau_0)}{\alpha_3^2+\omega_{p_2}^2}$$
$$+\frac{I_3\omega_{p_2}\sin(\omega_{p_2}\tau_0)}{\alpha_3^2+\omega_{p_2}^2} \,. \tag{6g}$$

This set of equations is solved by a suitable computer program and six out of seven constants were precisely determined. The last one required a slight adjustment. With these values the relaxation curve is expressed as

$$I_{\mathrm{ph}}(t)=5.24\times10^{-8}(1-e^{-t/0.0015})+1.24\times10^{-8}(1-e^{-t/0.0095})-u(\lambda)\times0.247\times10^{-8}(1-e^{-(t-4.9\times10^{-5})/0.0001}) \,. \tag{7}$$

Here the current was measured in A and the time in S. By using Eq. (7), the relaxation curve was constructed and is given in Fig. 1(b). Comparison between Figs. 1(a) and 1(b) shows that for the major part of the curve there is an excellent agreement. This is also true for decay curves (not shown here).

This is the first time that the relaxation photoresponse is precisely explained with the help of the parameters obtained uniquely with the present method of analysis (not only the form but also the numerical values).

V. DISCUSSION

By using the proposed technique of analysis, it has been found that the rise curve can be understood with two nondelayed and one delayed time constants and their values are 1.5×10^{-3}, 9.5×10^{-3}, and 10^{-4}s.

The major time constant in CdS, due to band-to-band recombination process, is found to be between 10^{-2} and 10^{-4} s.[1–3] The obtained value in the present investigation 1.5×10^{-3} s lies in the reported range.

The photoconducting device is generally made from copper (or selenium)-doped CdS powder and therefore, it is proper to compare the trap dominated time constant for these samples with the estimated one. Klosterboer *et al.*[9] have investigated the time constant by microwave photoconductivity and found that it is of the order of 1.1×10^{-3} s which is in close agreement with the value obtained from the present technique (9.5×10^{-3} s).

The term corresponding to the delayed component in Eq. (7) is negative. Generally, in the simulation process of the rise curve, the negative term is not included. Its presence can be understood by considering the rate of flow of the electrons between the conduction band and the traps:[10]

$$\frac{dn_c}{dt}=C_n(N_t-n_c)n-n_c/\tau_3 \,, \tag{8}$$

where n_c is the number of occupied traps, C_n is the capture cross section, N_t is the total number of traps and, therefore $(N_t - n_c)$ is the number of unoccupied traps. If it is assumed that the number of electrons in the conduction band and the number of empty traps are much higher than the number of occupied traps, n, then the first term of Eq. (8), which represents the rate of filling of traps, is practically constant as compared to the variation in n_c. In this case, the solution of Eq. (8), which represents the time-dependent behavior of occupied traps, can be written as

$$n_c = (n_c)_{\max}(1 - e^{-t/\tau_3}) . \tag{9}$$

Equation (9) shows the approximate rate at which the electrons from the conduction band are reduced and the traps are filled. After multiplying both sides of Eq. (9) by the electron charge, e, the mobility μ_n and the life time τ_3, Eq. (9) becomes

$$I_{\mathrm{ph}} = I_{\max}(1 - e^{-t/\tau_3}) . \tag{9a}$$

Thus, Eq. (9a) represents the contribution of the photocurrent due to the traps. As the trap filling rate is much higher than the reemission rate, the contribution is negative. This is exactly what is observed with the present analysis and is reflected in Eq. (7).

Reemission rate of the capture electrons is given by

$$\tau_3 = \tau_e \exp(-E_B/kT) \tag{10}$$

where E_B is the activation energy of the traps. The preexponential factor is the reciprocal of the "attempt to escape" frequency and it depends upon the characteristics of the traps, thermal velocity of the trapped carriers, and the effective mass. Here, τ_e is a constant whose value from other experimental reported results have been estimated and is 10^{-7}-10^{-8}s.[3]

In CdS, there exists several types of traps, one of them is located at 0.29 eV.[2] Using this value of activation energy and the value given above for the preexponenetial factor, the τ_3 has been calculated and found to be 7×10^{-4}-7×10^{-3}s, which is also in very good agreement with the value obtained from the present analysis ($\tau_3 \cong 10^{-4}$ s).

The magnitudes of the components of the photocurrent originated from different processes can be appreciated from Eq. (7). The major contribution (52.4 nA) comes from the direct-band-gap process with a time constant of 1.5 ms. The trap-assisted contribution, as expected, is less than the previous contribution and is approximately 23% with a time constant of 9.5 ms. The contribution from the traps whose activation process is delayed is significantly less and is about 5% of the contribution from the band-to-band process (1.5% of the total value of the photocurrent) and has a time constant of 0.1 ms.

In this way we have analyzed several rise and decay signals for different intensities of radiation. For all of these curves the agreement between calculated and digitized values obtained experimentally is excellent. Current investigation confirms that these time constants provide meaningful information about the important parameters of the kinetics of the charge carriers. The details will be published shortly. The present investigation indicates the validity of the proposed technique.

VI. CONCLUSIONS

By using the real or imaginary parts of Fourier transform, the relaxation curves recorded in photoconductivity have been analyzed and time constants and amplitudes were estimated uniquely without previous knowledge of the trap parameters. The analysis shows that in CdS, the photocurrent consists of three major components and their relative values will help to understand several hidden aspects of photoconductivity.

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[1] S. M. Ryvkin, *Photoelectric Effects in Semiconductors* (Consultants Bureau, New York, 1964).

[2] R. H. Bube, *Photoconductivity of Solids* (Wiley-Interscience, New York, 1960).

[3] A. Rose, *Concepts in Photoconductivity and Allied Problems, Interscience Tracts on Physics and Astronomy* (Wiley-Interscience, New York, 1963).

[4] J. P. McKelvey, *Solid State Semiconductors Physics* (Harper and Row, New York, 1966).

[5] I. Turek, Phys. Status Solidi A **62**, K45 (1980).

[6] R. Dyson and I. Isenberg, Biochem. **10**, 3233 (1971).

[7] N. V. Joshi and J. Martin, Phys. Lett. **113A**, 6 (1985); 318 **113A**, (1985).

[8] N. V. Joshi and S. Swanson, J. Solid. State Electronics **30**, 105 (1987).

[9] D. H. Klosterboer, W. L. Meissner, and M. R. V. Sahyun, J. Appl. Phys. **54**, 5161 (1983).

[10] J. S. Blakemore, *Semiconductor Statistics* (Pergamon, New York 1962).