# PHOTOCONDUCTIVITY AND TRANSPORT KINETICS IN ZINC OXIDE BINDER LAYERS

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## *Abstract*

*Photoconductive binder layers were fabricated using zinc oxide, ZnO, as active material, and dissolved polyvinyl alcohol, PVA, as the binder. The matrices employed were made of a constant total mass of 10g for the ingredients in each mixture in the ratio (1- x) ZnO: xPVA with $x = 0.1, 0.2, 0.3, 0.4, 0.5$. The layers showed a photocurrent, $I_{ph}$, to dark current, $I_d$, ratio of $10^4$, and the illumination dependence of photoconductivity is of the power law $I_{ph} = kL^n$, where k and n are dependent on the intensity, L. The log-log plot of the time variation of the recombination current shows two distinct domains with additive slopes of 1.84, indicative of fractal behaviour of a disordered structure. The carrier lifetime, $t_r$, obtained from the transition region is about 180s, which is too long, making the layers useless for counting devices.*

***Key words:*** *Photoconductivity, transport kinetics, binder layers, fractals.*

## Introduction

The charge carriers in solids occupy energy states which are available according to the laws of quantum mechanics. These energy states are in two broad bands, i.e. the valence and conduction bands, which are separated by an energy gap. These carriers interact very strongly with the lattice, and in the absence of external excitation, the lattice and carrier temperatures are equal. The free electrons and holes existing under this condition are called equilibrium carriers.

The charge carriers can gain energy to overcome the energy gaps between allowed bands, or between local impurity levels and these bands. If an electron in the valence band acquires enough energy and moves to the conduction band, a hole is created in the valence band. The application of external energy amplifies the process of carrier generation. The increase in the electrical conductance of the material due to external excitation by light is known as photoconductivity. When carriers are generated by external excitation, the energy used is retained mainly by the electrons, while the equilibrium energy of the crystal lattice remains practically unchanged. When the external excitation is removed, there occurs relaxation of the non-equilibrium carriers

through recombinations.

Photoconductivity has been observed in a wide range of materials, and has been utilised in various devices (Bube, 1974). Photoconductivity in single crystals is characterised by high gain and small photogenerated carrier lifetimes (Sze, 1996). This is due to a high degree of order in the single crystal. However, single crystals are expensive to grow, and devices employing them are not cheap. The binder layer is an inexpensive means, and this paper presents studies on zinc oxide/polyvinyl alcohol photoconductive binder layers.

## Theory

An important parameter for a photoconductor is the gain, G, defined by (Bube, 1967)

$$G = \frac{\tau}{t_r} \qquad (1)$$

where is the lifetime of free carrier, and $t_r$ is the transit time for this carrier. For a high gain, $t_r$ should be small. Factors that increase $t_r$ are the traps which decrease the effective mobility of the carriers by a factor $(1 + \tau_g/\tau_t)$, where $\tau_t$ is the average trapping time and $\tau_g$ is the thermal regeneration time. This function is approximately equal to $(1 + \exp(E/\kappa T))$,

where A is a constant dependent on the number of traps, E is the trap depth, $\kappa$ is Boltzman's constant, and T is the temperature of the sample. The traps in disordered samples have been widely studied (Scher and Montroll, 1975; Schlesinger, 1988), and their distribution is found to be fractal. The binder layer is a disordered system in which trapping potentials occur at ZnO grain boundaries, and ZnO/PVA interfaces. There is dispersion in the distances between nearest neighbour trapping sites, and dispersion also exists in the trap depths. The carrier therefore executes random walk in the sample, and the step length is stochastic. If under a continuous time random walk approximation (Schlesinger, 1996), we make a transformation from step length to hopping time, t, i.e. the carrier arrival time between successive trap sites, the probability that the hopping time lies between t and t + dt is (t)dt, where (t) is the probability density. If a carrier does not hop, it is trapped.

Complimentary to (t) is (t), the probability density that the carrier remained trapped until time t. We have that

$$\phi(t) = 1 - \int_0^t \psi(\tau)d\tau \qquad (2)$$

Let the probability density of a hop between the trap at site 1 and that at the nth site in time t be (t), then

$$\psi_n(t) = \int_0^t \psi_{n-1}(t-\tau)\psi(\tau)d\tau \qquad (3)$$

The Laplace transform is

$$\psi_n^*(s) = \int_0^s \psi_n(t)\exp(-st)dt = \sum_{n=0}^{\infty} (-1)^n s^n <t^n> \qquad (4)$$

The moments of the probability density is defined as

$$<t^n> = \int_0^{\infty} t^n \psi(t)dt \qquad (5)$$

Equation (4) exists only if the moments, , are finite, a situation which holds for Gaussian distribution. In this case,

$$\psi(t) = \lambda \exp(-\lambda t) \qquad (6)$$

This is the form of the probability density in an ordered structure. The probability in a disordered structure is of the form (Schlesinger, 1996)

$$\psi(t) = \frac{1-a}{a} \sum_{n=1}^{\infty} a^n b^n \exp(-b^n t), \qquad (7)$$

for b<a<1

where each level, n, has a power-law weight, $a^n$ and a release time weight, $b^n$.

The mean of such distribution is

$$<t> = \frac{1-a}{a} \sum_{n-1}^{\infty} \left(\frac{a}{b}\right)^n = \infty \qquad (8)$$

It is then observed that equation (4) is not valid in a disordered structure. The Laplace transformation of equation (7) gives

$$\psi^*(s) = a\psi^*\left(\frac{s}{b}\right) + \frac{b(1-a)}{s+b} \qquad (9)$$

The second term on the right hand side of equation (9) is analytic, therefore, any non-analytic behaviour of  must be due to the homogenous term, . If we write

$$\psi_h^*(s) = a\psi_h^*\left(\frac{s}{b}\right) \qquad (10)$$

where h means homogeneous, the solution to equation (10) is

$$\psi^*(s) \approx s^{\beta}K(s) \text{ with } \beta = \frac{\ln a}{\ln b} \qquad (11)$$

and K(s) is a function periodic in ln s with period ln b. The term in equation (11) is missing from equation (4), and it is now included to obtain

$$\psi^*(s) = 1 - s^{\beta}K(s) + \frac{1-a}{a} \sum_{n=1}^{\infty} \frac{(-1)^n as^n}{b^n - 1} \qquad (12)$$

$$\approx 1 - s^{\beta} + O(s), \text{ as } s \to 0$$

Then,

$$\psi(t) \approx t^{-1-\beta} \text{ as } t \to \infty \qquad (13)$$

When is governed by a fractal-time random process. If and , then , is finite, and Gaussian characteristics dominate.

When the random walk occurs with a bias (e.g. electric field) towards an absorbing plane, it is found (Scher and Montroll, 1975) that a transition region with a characteristic time, $t_r$, exists. The kinetics is then governed by the density probabilities,

and, $\quad \psi(t) \approx t^{-(1-\beta)}, \quad t < t_r \qquad (14)$

$$\psi(t) \approx t^{-(1+\beta)} \quad t > t_r \qquad (15)$$

Observe that irrespective of the value of $\beta$ the sum of the exponents in the above equation is -2.

## Materials and Methods

For each type of binder layer, a base volume of $50cm^3$ of water was used for mixing. PVA, of masses 1g, 2g, 3g, 4g and 5g were dissolved in the above volume of water, one mass value for a type of cell. The ZnO used was in the mass ratio $(1-x)$ ZnO: xPVA. To ensure that the PVA dissolved completely in the water, the mixture was gently warmed and stirred. The corresponding amount of ZnO was added to the PVA syrup and stirred until there was proper blending. This mixture was left to stand for some minutes, so that the trapped air bubbles escaped. The mixture was then poured on clean plates of aluminium of size 3cm x 3cm, and left to dry slowly for several hours. To ensure proper drying, the layers were placed in the oven and heated at $60\,^0C$ for 48 hours.

The methods for measuring photoconductivity and its relaxation have been described (Bube, 1974), and the set up is as shown in Fig. 1.
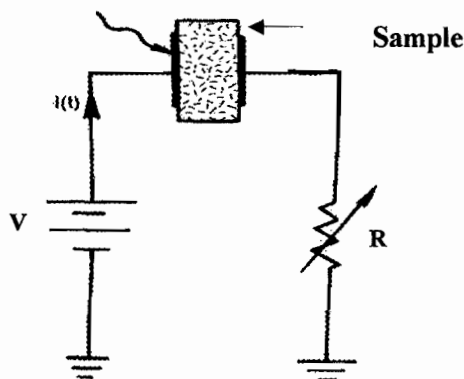


Fig.1: Photoconductivity measurement set-up

The characteristics of each cell were obtained by first measuring the dark current, $I_d$, under various bias voltages of 20V, 30V, 40V and 50V. The photoconductive characteristics were obtained by shinning light from a high intensity xenon lamp on the sample, via the transparent electrode. The peak photocurrent, $I_{ph}$, was measured. Moving the lamp away from the sample varied the intensity, L, of the incident light. The intensity at each position was measured with an International Light 1700 spectroradiometer, with the normalised intensities in the range 0.01 to 1.

The relaxation kinetics was obtained by switching off the illumination, and the residual current was measured as a function of time.

## Results and Discussion

The current traces for photoconductivity and relaxation are of the form shown in Fig. 2. These traces are similar for all the cells. The difference among the cells is more of a physical nature, in which the brittleness of the cells was found to increase as the fraction of ZnO in the mixture increased. A few drops of benzene in the mixture were found to act as a plasticizer, hence limiting the brittleness.
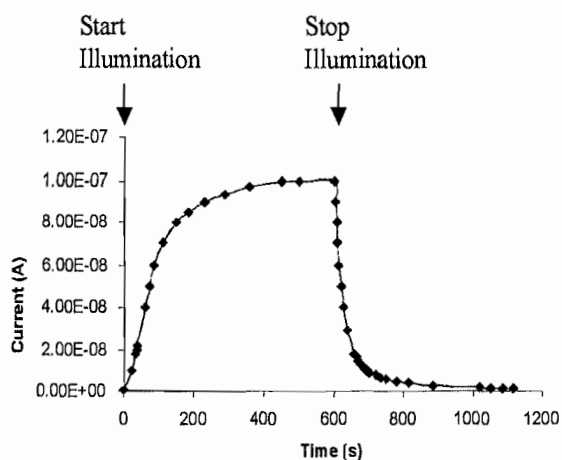


Fig. 2: Photoconductivity and relaxation kinetics

The ratio of $I_{ph}/I_d$ was of the order of $10^4$, indicating a suitable photoconductive gain for such devices as relays. However, the characteristic transit time, $t_r$, is about 180s, which is very large compared with the time for electronic processes in crystals. Therefore, the binder layer is not suitable in counting devices.

The slopes of the log-log plot for the decay of photocurrent in Fig. 3 are 0.75 and 1.09 for $t < t_r$ and $t > t_r$ respectively. The sum of the slopes is 1.84 in close agreement with the theoretical value of 2. This indicates that fractal processe control the kinetics in the binder layers.
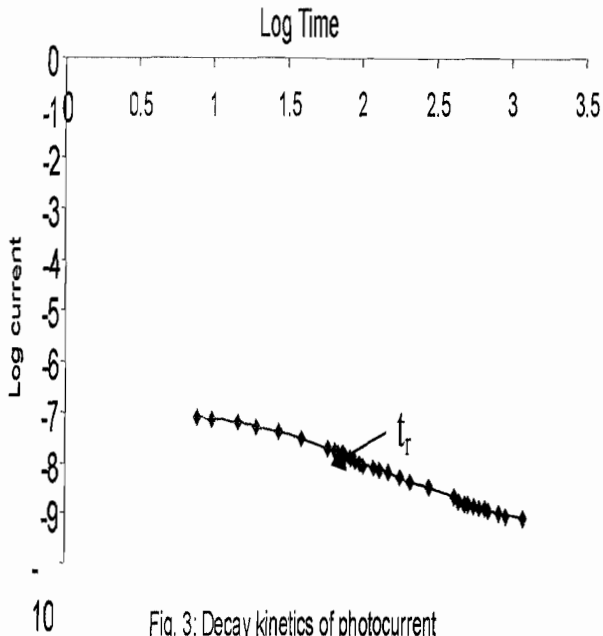


Fig. 3: Decay kinetics of photocurrent



Fig.4: Dependence of IphonL

The illumination dependence of photoconductivity is shown in Fig. 4. The graph is of power-law relationship, $I_{ph} = kL^D$, where k is a constant and D is an exponent. The power law suggests processes with fractal dimension of D, which is found to be illumination dependent. This may be due to the fact that in intervals of illumination, only few electronic processes dominate with respect to all others, and that the dominant ones may be different in various intervals (Stockman, 1971).

## Acknowledgement
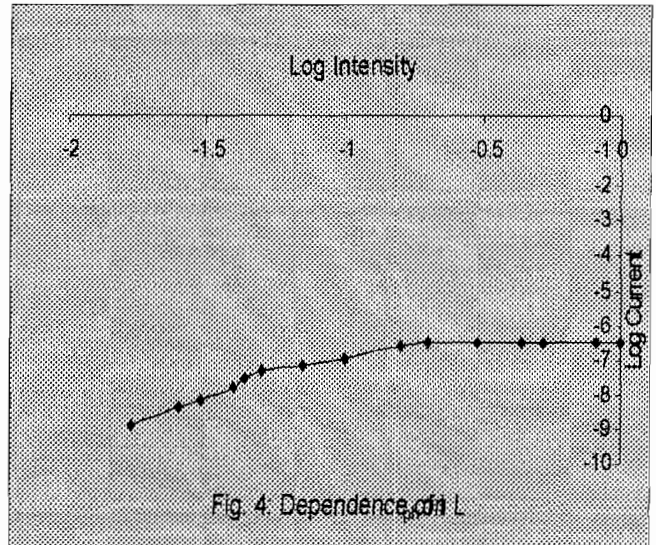
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