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# Photoconductivity and dark conductivity studies of (MgO–ZnO) mixed system

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**Abstract.** The photoconductivity and dark conductivity of (20% MgO–80% ZnO) mixed system in polystyrene binder layer have been studied and compared with (50% MgO–50% ZnO) and ZnO samples. For (20% MgO–80% ZnO) and (50% MgO–50% ZnO) samples, the dark current is found to be space charge limited at higher voltages. The photocurrent shows non-Ohmic behaviour at lower voltages and tends to saturation at higher voltages. For 100% ZnO system at higher voltages the photocurrent does not show any saturation effect and the dark current becomes linear. The change in photocurrent versus intensity curve from superlinear to sublinear indicates the presence of sensitizing centres near to the valence band and the existence of an exponential trap distribution in (20% MgO–80% ZnO) and (50% MgO–50% ZnO) samples. For 100% ZnO system, the photocurrent versus intensity curve changes from sublinear to linear indicating the presence of exponential trap distribution. Photocurrent decays more rapidly with increasing percentage of MgO in the mixed system. The X-ray diffraction pattern of these samples do not show formation of solid solutions.

**Keywords.** Semiconductors; photoconductors; photo-excitation.

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## 1. Introduction

Investigation of photoconductivity with respect to a number of parameters such as temperature, light intensity, voltage, energy of illumination etc. gives us useful information about the material. The temperature dependence of dark and photocurrent gives a fairly good information about the localized defect states and energy depth of Fermi-level. On the other hand, the nature of current versus intensity curve gives an idea about the charge trapping and recombination processes taking place inside the material. The rise and decay can be used to determine the nature of distribution of traps and recombination centres.

Although a lot of literature does exist on the photoconducting properties of single crystals, (Bube 1964; Mark 1964; Shmilevich *et al* 1981) relatively fewer measurements have been made in binder layers. Photoconducting properties of binder layers differ considerably from those of single crystals due to large surface to volume ratio and current flow through inter-particle contacts. The measurements with binder layers are simple and economical.

Photoconducting properties of a large number of materials have been investigated by several workers (Pillai *et al* 1983; Nair *et al* 1987; Kenawy and Zayed 1990; Queisser 1990). Extensive studies of photoconduction in II–VI compounds have been carried

out (Day 1953; Melnick 1957; Chan and Hill 1976; Gupta *et al* 1978). (MgO–ZnO) system responded for photoelectret (Sadhana Devi 1990) studies. Further, MgO (Woods and Wright 1955) and ZnO (Lehmann 1968) both act as luminescent materials. Therefore, it was interesting to study photoconductivity in (MgO–ZnO) systems which is the subject matter of present paper.

## 2. Experimental

The (MgO–ZnO) mixed systems were prepared by taking the high purity base materials i.e. MgO and ZnO in different proportion by weight and firing them at 700°C in a cylindrical furnace in air atmosphere for 1 h.

The fired material was mixed in polystyrene binder and sandwiched between a plane polished aluminium plate and a conducting glass plate. The cells were deposited on an area of about 1 $cm^2$ with thickness, $\sim 0{\cdot}04$ cm.

The cell was kept in a dark box with a hole on its top surface. The upper surface of the cell could be exposed by radiation as obtained from a 300 W mercury lamp. Intensity over the cell surface was varied by changing the slit width. The area of the illuminated surface was always kept greater than the area of the cell. A stabilized d.c. field (from 3·5 V/cm to 125 V/cm) was applied across the cell and the photocurrent was measured by a nanoammeter. For temperature variation, the cell was kept in an oven.

## 3. Results and discussion

### 3.1 *X-ray diffraction*

X-ray diffraction patterns studied for pure MgO, pure ZnO and mixed systems do not show any shift in diffraction lines (figure 1). The various $d$-values have been given in table 1. It shows that no solid solution formation takes place under experimental conditions. Therefore, MgO probably provides defects in ZnO lattice, thereby controlling the properties. The properties of ZnO (Harrison 1954; Melnick 1957), MgO (Weber 1951; Day 1953) base materials are different from that of the mixed (MgO–ZnO) system.

The (20% MgO–80% ZnO) combination fired at 700°C for 60 min shows maximum photosensitivity amongst all other mixed systems with different compositions. The photoconducting properties of (20% MgO–80% ZnO), (50% MgO–50% ZnO) and pure ZnO systems have been studied with respect to various parameters. The results are as follows.

### 3.2 *Effect of field*

Variation of dark current and photocurrent with voltage are shown in figure 2 on a log–log scale. For 100% ZnO sample, $\log I$ versus $\log V$ curves are straight lines but the lines have different slopes for lower and higher voltages. Thus the variation may be represented by $I \propto V^r$ where $r$ is the slope of any straight line section. For mixed systems, the $\log I$ versus $\log V$ curves are straight lines only at lower voltages.

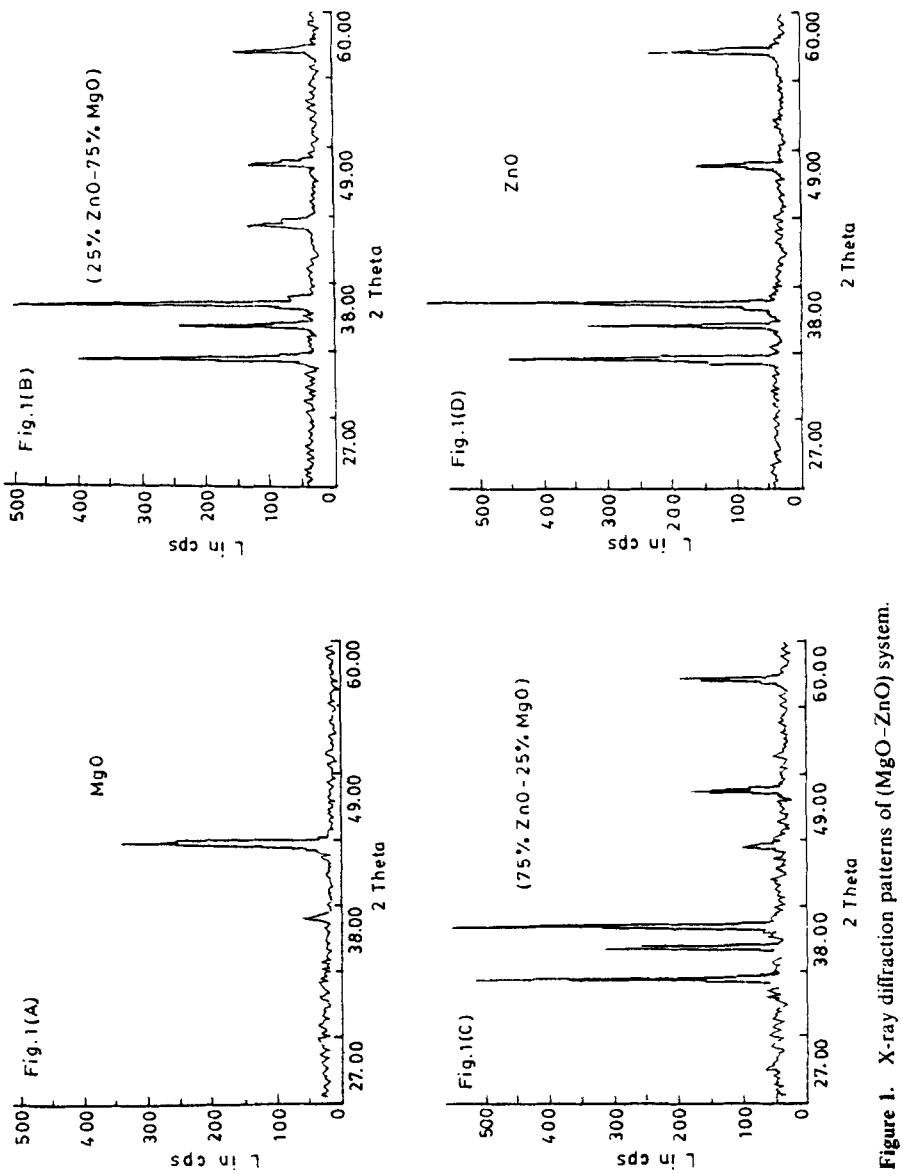


**Figure 1.** X-ray diffraction patterns of (MgO–ZnO) system.

**Table 1.** *d*-values.

| Composition | 2θ(deg.) | *d*(Å) | $I_{max}$(relative) |
|---|---|---|---|
| 100% MgO | 42·926 | 2·1048 | 256·0 |
| 75% MgO–25% ZnO | 31·814 | 2·8105 | 384·7 |
| | 34·473 | 2·5996 | 258·7 |
| | 36·302 | 2·4727 | 598·0 |
| | 42·888 | 2·1070 | 67·3 |
| | 47·594 | 1·9091 | 131·3 |
| | 56·633 | 1·6239 | 157·3 |
| 25% MgO–75% ZnO | 31·844 | 2·8079 | 402·0 |
| | 34·574 | 2·5922 | 284·0 |
| | 36·346 | 2·4698 | 565·3 |
| | 42·827 | 2·1099 | 127·3 |
| | 47·661 | 1·9065 | 128·7 |
| | 56·639 | 1·6238 | 151·3 |
| 100% ZnO | 31·811 | 2·8108 | 462·0 |
| | 34·485 | 2·5987 | 322·0 |
| | 36·307 | 2·4724 | 677·3 |
| | 47·598 | 1·9089 | 166·7 |
| | 56·538 | 1·6264 | 188·0 |

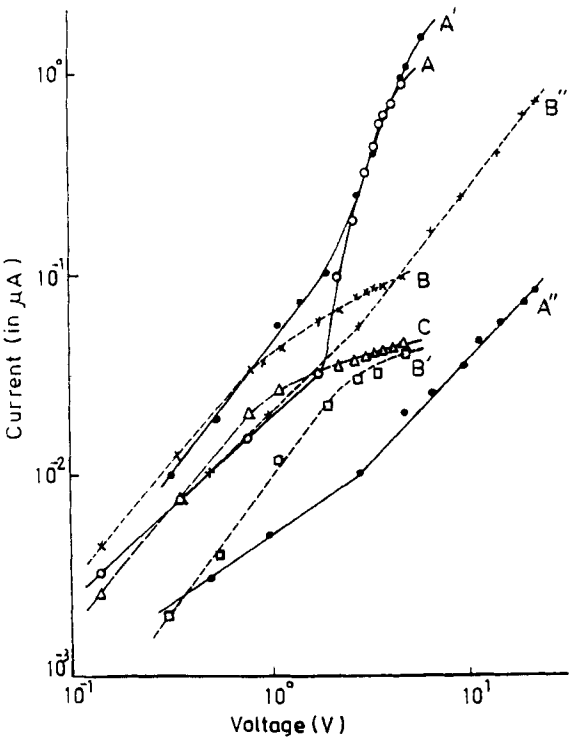


**Figure 2.** Variation of dark current and photocurrent with applied voltage. A, A′ and A″, dark current for (20% MgO–80% ZnO), (50% MgO–50% ZnO) and 100% ZnO systems respectively; B, B′ and B″, photocurrent at 4050 lux for (20% MgO–80% ZnO), (50% MgO–50% ZnO) and 100% ZnO systems respectively; C, photocurrent at 1200 lux for (20% MgO–80% ZnO) system. (Temperature = 22·5°C).

Behaviour of (20% MgO–80% ZnO) and (50% MgO–50% ZnO) samples is nearly same but different from pure ZnO. At higher voltages, the dark current varies with voltage according to a power index greater than 2 for (20% MgO–80% ZnO) and (50% MgO–50% ZnO) samples but varies linearly for pure ZnO system. This shows that the current flow through (20% MgO–80% ZnO) and (50% MgO–50% ZnO) systems is limited by space charge at higher voltages. The current flow through an insulator is limited by space charge when carriers in excess of those present in thermal equilibrium can be injected through a contact. At low voltages, the injection of charge carriers is not possible. However, at high voltages, the currents are no longer determined by the carrier densities that were present without any field. The currents at these higher voltages arise from a space charge of excess carriers injected from one of the electrodes. This is called space charge limited current. If the material has traps, then this current will also be determined by traps. This trap-limited space-charge limited current varies with voltage, according to a power index greater than 2 (Smith and Rose 1955). However, for 100% ZnO, injection of charge carriers is not possible in dark even at higher voltages.

The photocurrent shows non-Ohmic ($r > 1$) behaviour in the lower voltage region but tends to slight saturation at higher voltage range for (20% MgO–80% ZnO) and (50% MgO–50% ZnO) systems. For 100% ZnO system, the photocurrent becomes non-linear only at higher voltages studied without showing any saturation effect. Non-Ohmic behaviour of the photocurrent suggest that some carriers are being injected into the material as explained earlier. Slight saturation in photocurrent has also been explained by Pillai *et al* (1985) by using the concept of class II states. We assume that, among the various imperfections present, there are two kinds of dominant states (class I and class II) in the forbidden gap. Class I consists of states which have roughly similar cross-section for both electrons and holes and lie near the middle of the gap. Class II states are close to the valence band and have higher capture cross-section for holes than for electrons (Rose 1963). The existence of class II trapping sites can explain the slight saturation effect observed in the $I_p$ versus $V$ curves at higher intensities.

In the absence of illumination, there will be only one Fermi-level for both holes and electrons. Since (MgO–ZnO) is a *n*-type material, the Fermi level will be closer to the conduction band. However, in the illuminated material, there will be two Fermi-levels, one corresponding to electrons and the other one corresponding to holes (Bube 1967). We consider that at a particular light intensity and voltage the position of the Fermi-levels are such that they have just converted all the class II states into recombination levels. The effect of the additional electrons injected into the material by the additional voltage will be to raise the Fermi level upwards towards the conduction band. This would cause some of the class II centres to act as hole traps again, leading to desensitization and the decrease in electron life time with increasing voltage. This could account for the saturation-effect in curves B, B′ and C in figure 2.

### 3.3 *Effect of intensity*

The variation of photocurrent with light intensity at different voltages is shown in figure 3 on a log–log scale. Nature of curves for (20% MgO–80% ZnO) and (50% MgO–50% ZnO) mixed systems is nearly same but different from pure ZnO.

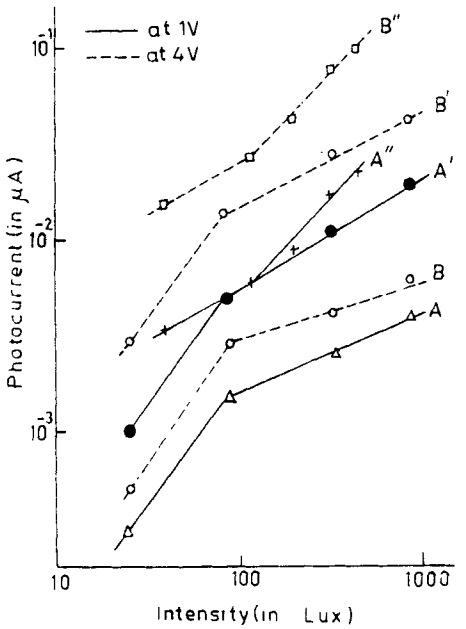


**Figure 3.** Variation of photocurrent with light intensity at different voltages. A, A' and A'', for (50% MgO–50% ZnO), (20% MgO–80% ZnO) and 100% ZnO samples respectively; B, B' and B'', for (20% MgO–80% ZnO), (50% MgO–50% ZnO) and 100% ZnO samples respectively (Temperature = 23°C).

Log of photocurrent versus log of intensity ($L$) curves are straight lines but the lines have different slopes for lower and higher light intensities. Thus the variation is given by $I_p \propto V^r$. The average value of $r$ is found to be 1·28 and 1·36 at lower intensities for (20% MgO–80% ZnO) and (50% MgO–50% ZnO) samples respectively and it is equal to 0·53 and 0·36 at higher light intensities for (20% MgO–80% ZnO) and (50% MgO–50% ZnO) samples respectively. However, for pure ZnO system average value of $r$ is found to be 0·1 at lower intensities and it is equal to 1 at higher light intensities. The change of photocurrent versus excitation intensity relationship from superlinear to sublinear nature for mixed systems can be explained on the basis of class I and class II centres (Pillai *et al* 1985).

At very low intensity of illumination and high temperature the position of the Fermi level may be such that class II states act as hole traps. By increasing light intensity the electron Fermi-level and hole Fermi-level are shifted towards the conduction and valence bands respectively. Thus converting some of the class II states into recombination centres which ultimately sensitizes the sample. This effect gives rise to superlinearity in $I_p$ vs $L$ curve. After full conversion of hole traps to recombination centres, the photocurrent should vary linearly with light intensity (Rose 1963) but the photocurrent varies sublinearly. This indicates that the distribution of class I centres is continuous and exponential in nature and these levels lie between the conduction band and the electron Fermi-level. As the intensity of illumination is increased the Fermi-levels of electrons and holes are separated apart more and more, thereby converting more of the class I centres to recombination centres. This process decreases electron lifetime with increasing intensity and gives rise to the sublinearity in the $I_p$ vs $L$ curve.

For 100% ZnO sample, the $I_p$ versus $L$ curve changes from sublinear to linear nature. This suggests a continuous trap distribution but rather exponential in nature between the lower edge of the conduction band and the electron Fermi-level. An increase in intensity would convert more of the trap levels to recombination levels thereby decreasing the electron lifetime and giving rise to observed sublinearity (Bube 1967). After full conversion, the photocurrent would vary linearly with light intensity.

### 3.4 *Temperature dependence*

The dark current ($I_D$) and photocurrent ($I_p$) are shown as a function of temperature in figure 4. We see that the dark current shows an increase with temperature up to 312°K and then decreases. Similarly $I_p$ increases up to 310°K after which it decreases.

If the material has traps, then a free electron captured in a trap can be thermally reexcited into the conduction band before capturing a free hole. This explains why $I_D$ increases with temperature. Thermal quenching of the dark current can be explained on the basis of class II type of centres. It may be assumed that the hole demarcation level lies somewhere in the region of the class II centres. An increase in temperature would cause Fermi level to come closer to the centre of the forbidden gap and simultaneously the demarcation level will rise upwards away from the valence band. This upward movement of the demarcation level would convert some of the class II centres from recombination centres to hole traps thus desensitizing the sample. This explains the thermal quenching of the dark current.

Increase in photocurrent ($I_p$) with temperature suggests that the Fermi-level shifts across an exponential trap distribution (Bube 1967). Thermal quenching of photocurrent can be explained on the basis of Rose model, i.e. when a photoconductor is illuminated, the two steady state Fermi-levels move apart towards their respective band edges. In this process a large number of traps are converted to recombination centres. The class II centres have higher capture cross section for holes as compared to electrons. Thus the photoconductor is so sensitized that the lifetime of conduction

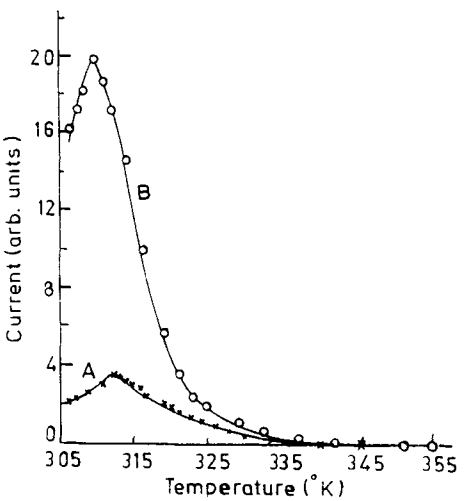


**Figure 4.** Variation of dark current and photocurrent with temperature. A, dark current at IV; B, photocurrent at 9050 lux and at IV.

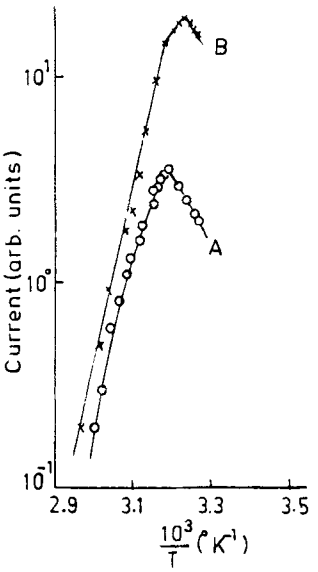


**Figure 5.** Arrhenius plots for dark current and photocurrent. A, dark current at 1V; B, photocurrent at 9050 lux and at 1V.

electrons increases. On the other hand, Fermi-level will be shifted away from the band-edge with the increase in temperature. This would convert sensitizing centres to traps. Thus the photoconductor is reverted from sensitive to insensitive state.

Arrhenius plots for $I_p$ and $I_D$ are shown in figure 5. The curves are straight lines having different slopes in different temperature regions.

The location of electron Fermi-level corresponding to any straight line section is calculated using the expression:

$$E_f = KT\log_e\left(\frac{N_c e\mu}{\sigma}\right) \tag{1}$$

where $\sigma/e\mu$ is the concentration of conduction band electrons, $\mu$ the mobility, $T$ the absolute temperature and $N_c$ is the concentration of levels present in the lowest $KT$ wide part of conduction band and is of the order of $10^{19}$ at room temperature.

In semilogrithmic plot of dark current versus $1/T$ curve, the thermal activation energy is found to be approximately 0·72 eV at the lower temperature side. By plotting log $I_p$ versus $1/T$, the average activation energy is found to be approximate 0·6 eV at the lower temperature side.

### 3.5 *Growth and decay curves*

Growth and decay of photocurrent for (20% MgO–80% ZnO), (50% MgO–50% ZnO) and 100% ZnO samples are shown in figure 6. Photocurrent decays more rapidly with increasing percentage of MgO in the system. Decay time for different compositions is given in table 2. For mixed systems, photocurrent decays very rapidly at high intensity. However, for (20% MgO–80% ZnO) system, photocurrent takes long time to decay, at lower intensity.

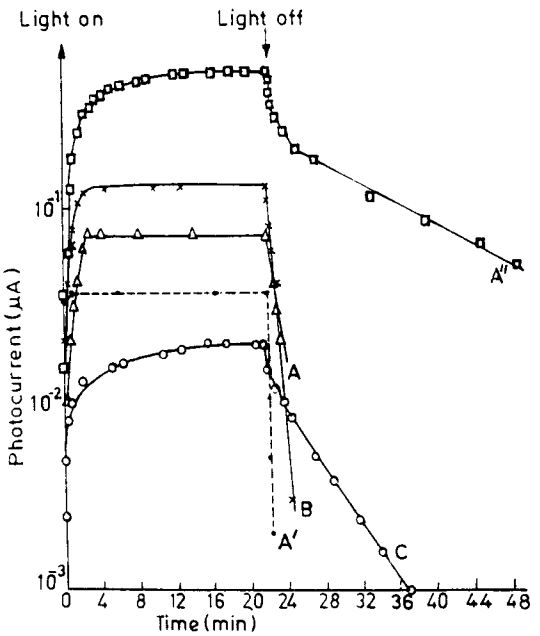


**Figure 6.** Rise and decay of photocurrent at different light intensities. A, A' and A'', at 4100 lux for (20% MgO–80% ZnO), (50% MgO–50% ZnO) and 100% ZnO systems respectively; C, at 110 lux for (20% MgO–80% ZnO) system; B at 9075 lux for (20% MgO–80% ZnO) system; (voltage = 4V and temperature = 17°C).

**Table 2.** Decay time of photocurrent at 4100 lux.

| Composition | Decay time (sec) |
|---|---|
| 100% ZnO | 120 |
| 20% MgO–80% ZnO | 40 |
| 50% MgO–50% ZnO | 12 |

The decay of photocurrent after the cessation of excitation depends strongly on the light intensity used. For very high light intensity, the density of free electrons is much larger than the density of trapped electrons and the decay would take place mainly due to the direct recombination of free electrons with holes in large cross-section recombination centres without any trapping process involved. This explains why decay takes place so rapidly at high intensities. However, for very low light intensities, the measured decay time will be determined by the ejection of electrons from deep traps. This explains why $I_p$ decays so slowly at low light intensities. For this reason, the decay curve at low light intensity, has been taken for the calculation of $p$-value (probability of an electron escaping from a trap) and trap depth ($E$).

The $p$-values corresponding to different exponentials have been calculated by the relation,

$$I = I_0 \exp(-pt) \tag{2}$$

where $I_0$ is the current at the moment light is interrupted and $I$ is the current at any instant of time.

The $p$-values for (20% MgO–80% ZnO) sample at low intensity of illumination and at 17°C are calculated to be $240{\cdot}1 \times 10^{-4}$, $32{\cdot}12 \times 10^{-4}$ and $28{\cdot}8 \times 10^{-4}$ for first, second and third exponentials respectively.

The theory of Randall and Wilkins (Randall and Wilkins 1945) for the emptying of traps assumes that the probability of an electron escaping from a trap is given by the relation,

$$P = S\exp(-E/KT) \tag{3}$$

where $S$ is the frequency factor, the "attempt to escape frequency", and the exponential term is a Boltzmann factor involving the trap depth $E$, and the temperature $T$. $S$ may be interpreted as the number per second that the quanta from crystal vibrations (phonons) attempt to eject the electrons from the traps, multiplied by the probability of transition from trap to the conduction band, and is of the order of $10^9$. The use of this equation requires the assumption that $S$ and $E$ are independent of temperature, and the electrons freed from traps are not retrapped, and that freed electrons undergo radiative, rather than dissipative transitions.

The trap depths corresponding to different exponentials can be calculated by using (2) and (3) and is given by

$$E = KT\left[\log_e S - \log_e \frac{\log_e I_0/I}{t}\right]. \tag{4}$$

The values of trap depths ($E$), at 17°C for 1st, 2nd and 3rd exponentials are 0·61, 0·66 and 0·66 eV respectively for (20% MgO–80% ZnO) sample.

## 4. Conclusions

The nature of curves is nearly same for mixed compositions, i.e. (20% MgO–80% ZnO) and (50% MgO–50% ZnO) samples but different from pure ZnO system. Dark current versus voltage curve shows the flow of trap limited space charge-limited currents inside the mixed compositions at higher fields. The existence of sensitizing centres near to the valence band and an exponential trap distribution are confirmed for mixed composition. For pure ZnO system, it is concluded that a continuous trap distribution exponential in nature exists below the lower edge of the conduction band. Decay of photocurrent takes place more rapidly with increasing percentage of the MgO in the system. X-ray diffraction patterns do not show the formation of solid solutions.

## References

Bube R H 1964 *J. Appl. Phys.* **35** 586
Bube R H 1967 *Photoconductivity of solids* (New York: John Wiley & Sons) Ch. 2 and 3
Chan D S H and Hill A E 1976 *Thin solid films* **35** 337
Day H R 1953 *Phys. Rev.* **91** 822
Gupta B K, Agnihotri O P and Raza A 1978 *Thin solid films* **48** 153
Harrison S E 1954 *Phys. Rev.* **93** 52

Kenąwy M A and Zayed H A 1990 *J. Mater. Sci. Mater. Electron* **1** 115
Lehmann W 1968 *J. Electrochem. Soc.* **115** 538
Mark P 1964 *J. Phys. Chem. Solids* **25** 911
Melnick D A 1957 *J. Chem. Phys.* **26** 1136
Nair P K, Nair M T S and Campos J 1987 *Solid Energy Mater.* **15** 441
Pillai P K C, Shroff N and Tripathi A K 1983 *J. Phys.* **D16** 393
Pillai P K C, Shroff N, Nand Kumar N and Tripathi A K 1985 *Phys. Rev.* **32** 8228
Queisser H J 1990 *Ann. Phys.* **47** 461
Randall J T and Wilkins M H F 1945 *Proc. R. Soc. (London)* **A184** 366, 390
Rose A 1963 *Concepts of photoconductivity and allied problems* (New York: Wiley), p. 43
Sadhana Devi 1990 *Investigation of photoelectret and related effects in mixed lattice of II–VI compounds* (PhD thesis, University of Allahabad, unpublished) p. 84
Shmilevich A M, Stys L E, Chemeresyuk G G and Serdyuk V V 1981 *Fiz. Tverd. Tela* (Leningrad) **15** 855 (1981 *Sov. Phys. Semicond. Engl. Transl.*) **15** 485)
Smith R W and Rose A 1955 *Phys. Rev.* **97** 1531
Weber H 1951 *Z. Phys.* **130** 392
Woods J and Wright D A 1955 *Proc. Phys. Soc. (London)* **B68** 566