

TECHNICAL NOTE R-237

CONDUCTIVITY PHENOMENA IN
POLYCRYSTALLINE ZINC OXIDE FILMS

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ABSTRACT

Conductivity in thin zinc oxide films is found to increase as film thickness increases. An empirical relation expressing this phenomena is given along with a physical explanation. Time rate change of conductivity data and voluntary response due to incremental changes in pressure are briefly discussed.

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INTRODUCTION

Polycrystalline zinc oxide, as a pigment in thermal control coatings presently in use on space vehicles, has a significant role in the space effort. However, the optical and electrical properties of zinc oxide are subject to change when environmental conditions are that of low ambient pressure (vacuum) and solar irradiation. As a part of the continuing effort to better understand the mechanism of this undesirable phenomena, some recent experimental results concerning the effect of sample thickness upon sample conductivity are presented. Time rate change of conductivity data and voluntary response as a function of pressure data are also briefly discussed.

The experimental results are interpreted in the framework of a tentative model as shown in Figure 1. In this model, it is shown that

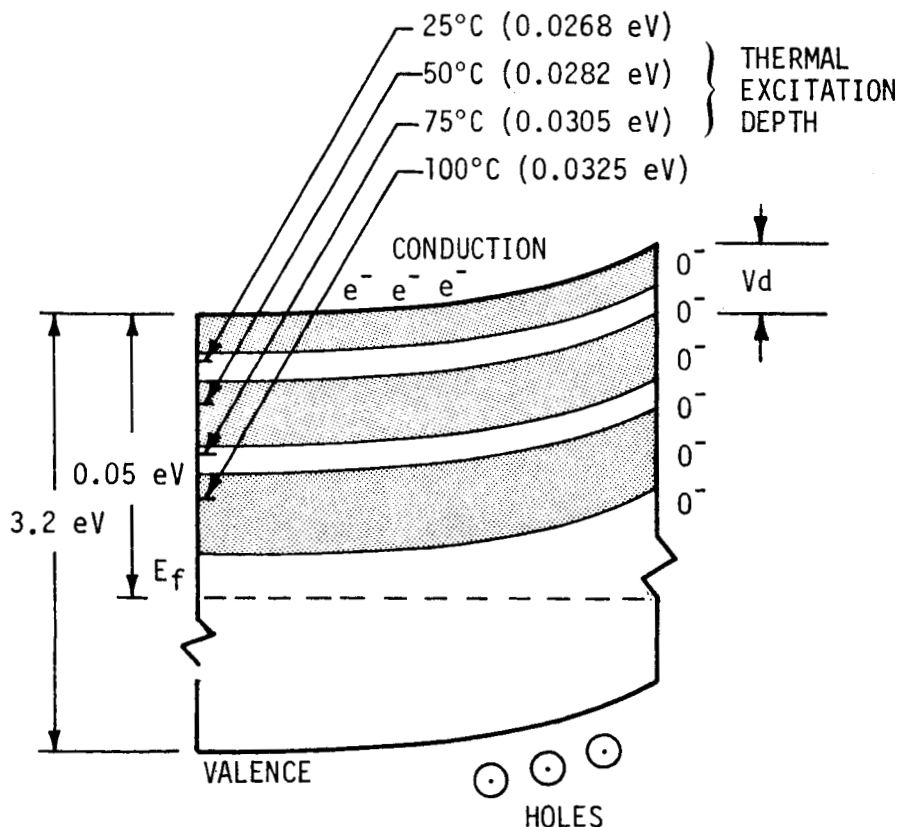


Figure 1. Solid State Energy Model of Polycrystalline Zinc Oxide

atomic oxygen localizes charge carriers (electrons) at the surface, generating an electrostatic field which causes a depletion layer of depth ℓ in the material bulk. Charge carriers are thermally excited from donor levels lying near the conduction band; the degree to which these charge carriers are generated and arrive at the surface is deterred by the upward bending of the conduction band $[V_d(x)]$.

Photoconduction occurs when incident photons create electron-hole pairs at the valence level, exciting the electron to the donor or conduction level. The hole is accelerated by the surface field to the surface where the electron bound to the monatomic oxygen is taken by the hole. The oxygen, thus neutralized, is now only physically bound and in vacuum desorbs from the surface. The electron previously liberated in the electron-hole creation now becomes a charge carrier as $V_d(x)$ is decreased by the oxygen liberation process.

EXPERIMENTAL RESULTS

Some relevant data concerning the relationship of conductivity in zinc oxide films to film thickness has been experimentally noted. The conductivity measurements were made in vacuum ($\sim 10^{-7}$ torr) with the zinc oxide film under low intensity 3650 angstrom irradiation.

Prior to discussion of conductivity-thickness data, it is relevant to show that the maximum Shottky barrier depth due to the electrostatic field of bound surface charge is greater than the thickness of the thickest experimental film (1500 angstrom).

SHOTTKY BARRIER DEPTH

Using available information from published sources as well as information from previous experimentation the greatest possible depletion depth expected is to be calculated. Following the treatment of Mark¹, the largest concentration² of electrically compensated adsorbed oxygen ions, σ_m , is

$$\sigma_m = \left(\frac{2K \epsilon_0 N_+ V_d}{e} \right)^{\frac{1}{2}} \quad (1)$$

where

K - dielectric constant

ϵ_0 - permittivity of free space (8.85×10^{-14} farad / cm)

N_+ - the concentration of ionized donors in the depletion layer³
(9.0×10^{17} donors / cm³)

V_d - the barrier diffusion potential

e - the electronic charge (1.6×10^{-19} coulomb)

Hahn³ indicates ionized donor concentrations ranging from 1.6×10^{16} to 9.0×10^{17} donors / cm³. The larger number is taken since it conforms closely to the maximum number of charge carriers measured ($\sim 10^{17}$ carriers / cm³) in earlier experimentation.⁴ The dielectric constant, K, is taken⁵ as 12.

The maximum diffusion potential, hence the greatest depletion depth, is then given from Equation 1 by

$$V_d = \frac{\sigma_m^2 \ell}{2K \epsilon_0 N_+} = 8.3699 \sigma_m^2 \times 10^{-26} \text{ V} \quad (2)$$

The maximum surface charge carrier density found by Heiland⁶ upon reduction of zinc oxide with atomic hydrogen was $\sigma_m = 10^{13} / \text{cm}^2$. Equation 2 then gives a diffusion voltage of 8.37 volts, a very high figure.

The greatest Shottky barrier depth is then given by⁷

$$\ell^2 = \frac{2K \epsilon_0 V_d}{eN_+} \quad (3)$$

Using the calculated maximum value for V_d , the maximum barrier depth expected in the zinc oxide is found from Equation 3 to be 3500 Å. Since the films to be discussed are not thicker than 1500 Å, the barrier depth is expected to influence the entire bulk of each crystallite.

CONDUCTIVITY AS RELATED TO THICKNESS

In Figure 2 is shown the vacuum photoresponse of four zinc oxide films in terms of film conductivity. The films are 425, 730, 1000, and 1500 angstroms thick. Although the slow response requires a long period

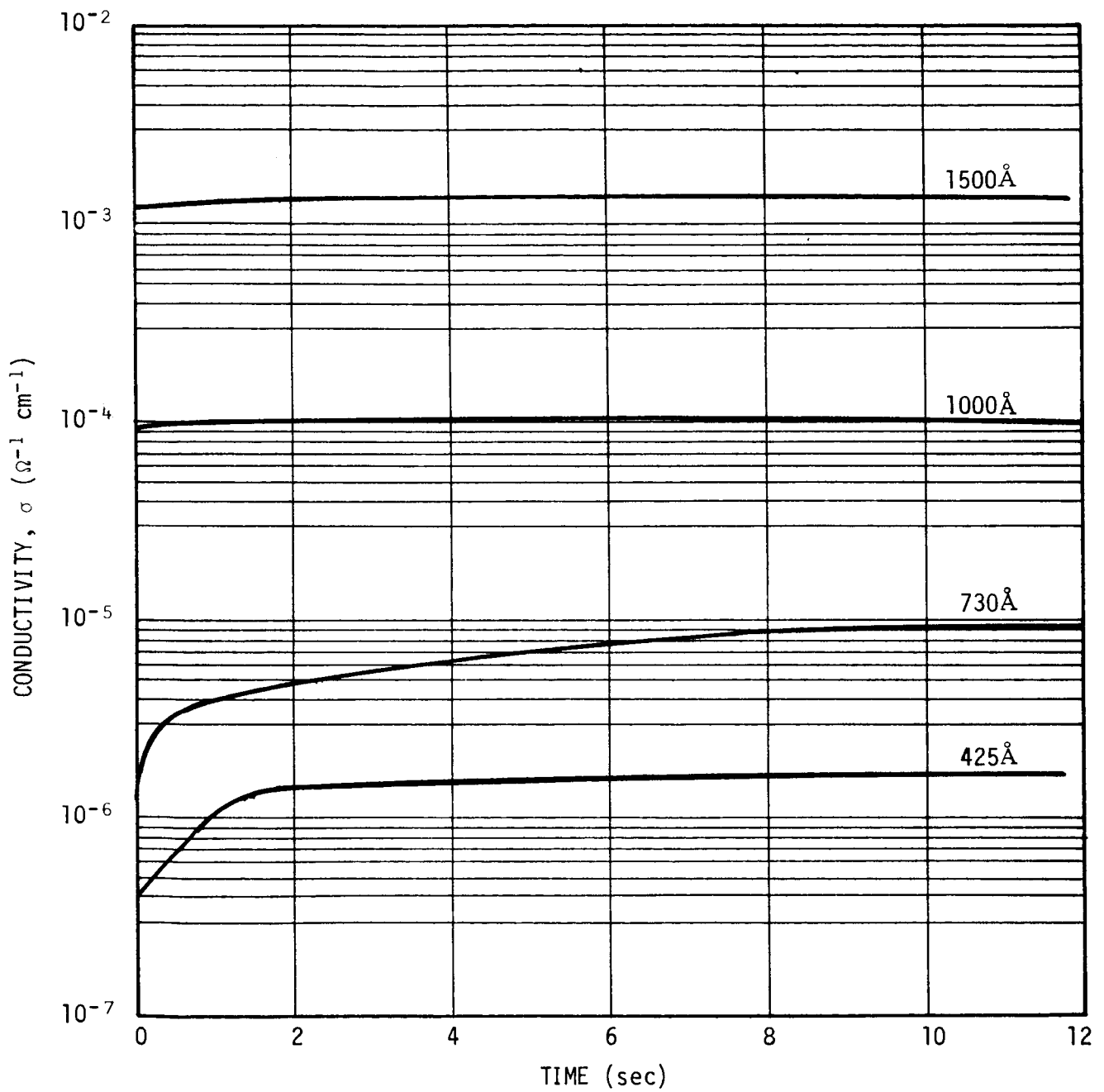


Figure 2. Conductivity as a Function of Duration of 3650 Å Irradiation in Four Zinc Oxide Films of Different Thicknesses

of time (hours to days) to come to an absolute equilibrium for a given constant irradiation level, the conductivity at ten seconds after initiation of irradiation is taken to be representative of the ultimate degree of film degradation.* To substantiate this assumption the time rate change of conductivity at $t = 10$ sec must be considered.

The time rate change of conductivity (TRC^2) is experimentally found to be (25°C , $\Delta t = 10$ sec) not greater than $3.5 \times 10^{-7} \Omega^{-1} \text{cm}^{-1} \text{sec}^{-1}$. Without consideration of the reduction of mean free path length of the free electrons by the physical dimensions of the crystallite, conductivity is given by

$$\sigma = ne\mu \quad (4)$$

where

- n - charge carrier density (cm^{-3})
- e - electronic charge (coulombs)
- μ - the electron mobility ($\text{cm}^2 / \text{V-sec}$)

The TRC^2 ($\dot{\sigma}$) is then given by

$$\dot{\sigma} = \dot{n}e\mu + ne\dot{\mu} \quad (5)$$

* This assumption should not be considered as contrary to the results given in Reference 4 for charge carrier density as a function of time data. The data in this report results from lower intensity, monochromatic irradiation. The reference data results from high intensity, full mercury arc spectrum irradiation.

From previous results⁴ $\dot{\mu} < -4 \text{ cm}^2 / \text{V-sec}^2$; hence the second term of Equation 5 can be neglected. TRC^2 is then expressed as

$$\dot{\sigma} = \dot{n} e \mu \quad (6)$$

Employing the maximum TRC^2 as noted above, ten seconds after initiation of irradiation \dot{n} is not greater than 2.2×10^{10} carriers / sec. Since the charge carrier density achieved⁴ is on the order of 10^{17} to 10^{18} carriers / cm^3 , by the time the generation rate has decreased to the above value, the conductivity at that temporal point is very near its maximum.

Figure 3 shows the relation between measured film conductivity and film thickness, the conductivity values being taken ten seconds after initiation of irradiation in vacuum. From the empirical data represented in Figure 3, the functional relationship between conductivity (σ) and thickness (t) in angstroms is

$$\sigma = 10^{0.0026 t(\text{\AA}) - 6.854} \quad (7)$$

This exponential increase of conductivity is not evidently a result of increasing mean free path length of the charge-carrying electrons. The conductivity-effective mean free path length dependency in thin films is linear as given by Leonard and Ramey⁸;

$$\sigma = c n^{\frac{2}{3}} \lambda_{\text{eff}} \quad (8)$$

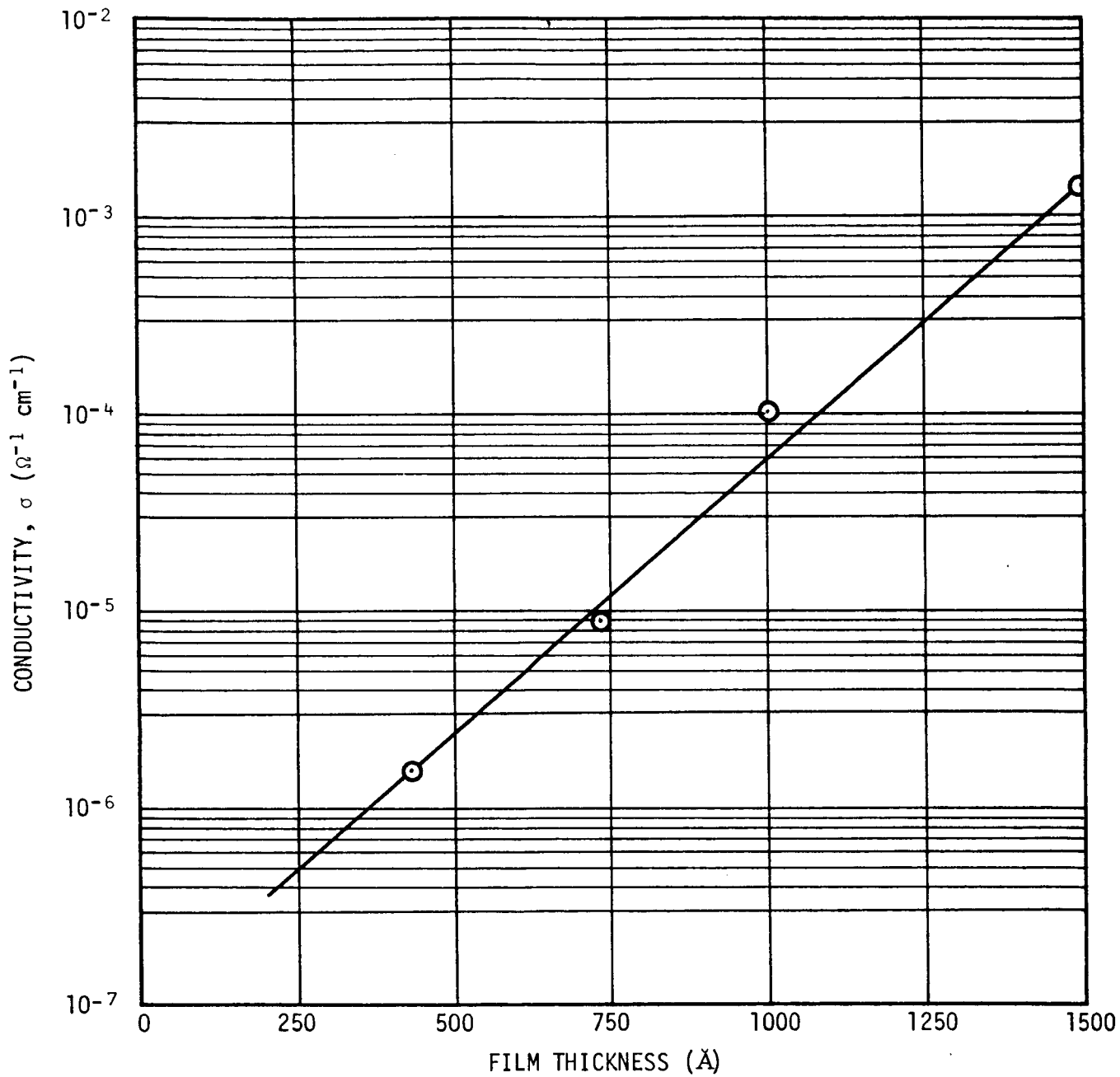


Figure 3. Conductivity as a Function of Film Thickness

In this expression c is a constant, n is carrier density and λ_{eff} is the effective mean free path length.

In view of the working model (Figure 1) the experimentally noted dependency of conductivity upon film thickness has at least one plausible explanation. The individual crystallite dimensions⁶ are approximately 100 Å. The interfaces of the individual grains are sealed to some extent from the ambient oxygen as shown in Figure 4. Along these crystallite interfaces charge carriers (electrons) are thermally excited to the conduction band at room temperature. These charge carriers are not appreciably localized due to the paucity of available oxygen, even in an oxygen atmosphere.

Conduction in a film such as is shown in Figure 4 must be considered in two parts: the first few thousand angstroms from the exposed surface which is influenced by the electrostatic field of the surface charge and the remainder of the film which is not influenced by this surface generated field. In that part of the film where $V_d(x)$ is not zero, interface carrier density will be reduced by $V_d(x)$. This is evident by consideration of the form of the Fermi distribution function

$$F(E_c) = \frac{1}{\exp[(E_c + V_d(x) - E_f) / kT] + 1} \quad (9)$$

Since the absolute value of $V_d(x)$ decreases monotonically for increasing x , the conductivity is stratified in infinitesimal layers due to the transition probability of charge carriers to the conduction band. Conductivity at any given depth in the film could be expressed as (assuming mobility to be constant)

$$\sigma_x = e\mu \int_{E_c}^{\infty} Z(E) \frac{1}{\exp[(E + V_{dx} - E_f) / kT] + 1} dE \quad (10)$$

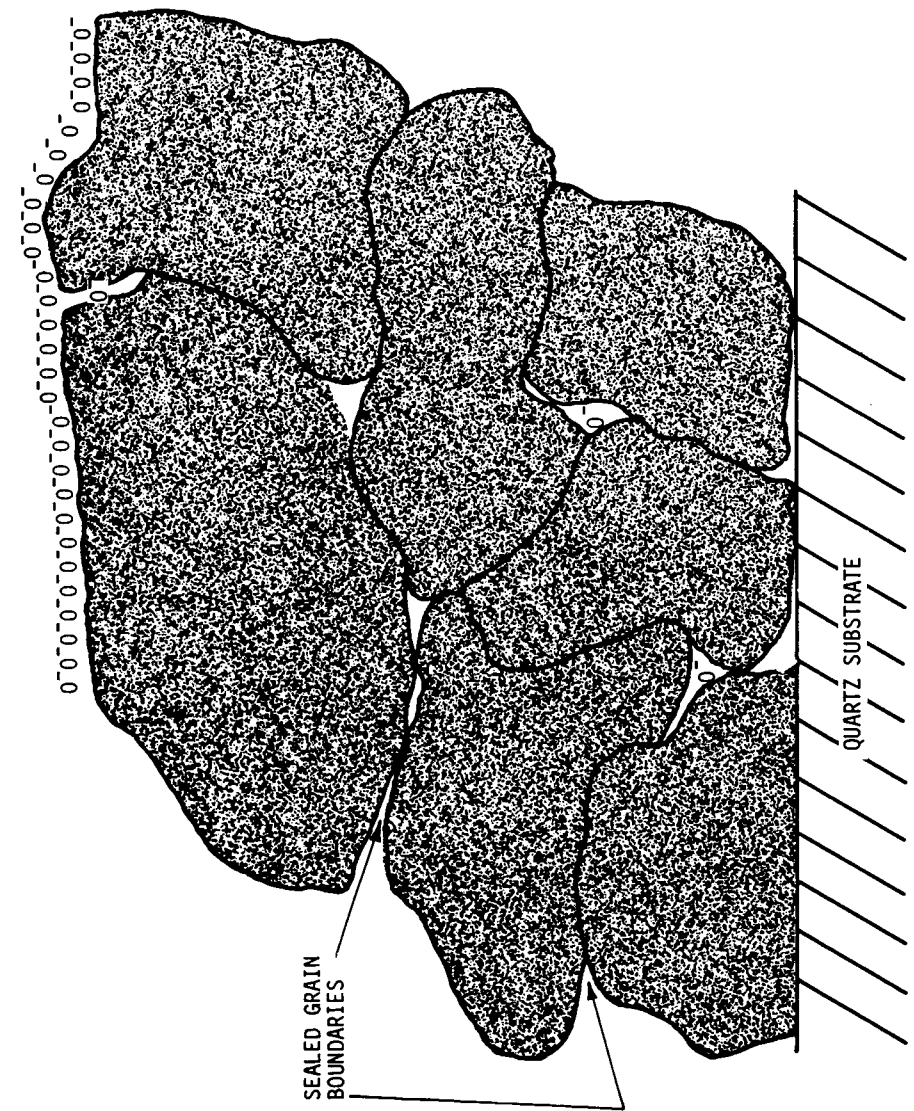
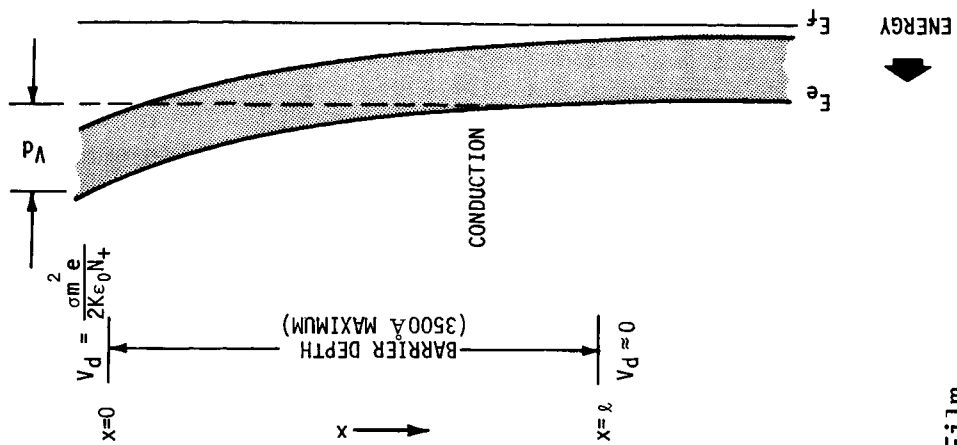


Figure 4. Cross Section of Polycrystalline ZnO Film Exhibiting Thickness Dependent Conductivity

In Equation 10 $Z(E)$ denotes number of possible states per unit volume. The average conductivity from $x=0$ to $x=l$ is then given by

$$\bar{\sigma} = \frac{e\mu}{a} \int_0^l \int_{E_c}^{\infty} Z(E) \frac{1}{\exp \{ [E + V_d(x) - E_f] / kT \} + 1} dE dx \quad (11)$$

For a film of thickness less than the barrier field depth (l) some conclusions can be drawn of the effect of varying film thickness upon measured (average) conductivity.

As the thickness of a film is increased, the average value of $V_d(x)$ influencing the transition probability of a charge carrier to the conduction band at the crystallite interfaces is decreased. The average equilibrium carrier concentration (hence conductivity) is then greater for thicker films. Since carrier concentration is dependent upon an exponential function of $V_d(x)$, it is then logical that conductivity increases exponentially with film thickness. This dependency is only in effect for film of depth dimensions no greater than maximum barrier depth ($\sim 3500 \text{ \AA}$).

That part of the film which is not influenced by the surface charge field ($x > l$), will exhibit conductivity characterized by donor density, temperature, crystallite size and availability of grain interface conduction paths. This part of the film should show only the slightest dependency of conductivity upon ambient oxygen. It is possible that some inter-crystallite voids would contain a small amount of oxygen as shown in Figure 4.

It is then expected that as film thickness is increased up to the surface charge field depth, the conductivity would increase exponentially with film thickness. For thicker films the conductivity would begin to approach asymptotically a maximum conductivity; this conductivity is

the conductivity expected of polycrystalline zinc oxide free of surface oxygen. Recent data obtained in this laboratory on films up to 10,500 angstroms thick indicate that this process does indeed take place.

TIME RATE CHANGE OF CONDUCTIVITY

The time rate change of conductivity (TRC^2) is examined in a 730 angstrom zinc oxide film at 10 and 20 seconds after commencement of irradiation and for 10 and 20 seconds after cessation of irradiation. These measurements were made for both 3650 angstroms and 4350 angstroms irradiation.

Figures 5 and 5a show TRC^2 as a function of film temperature for the degradation and recovery phases respectively. Irradiation of 3650 angstroms was used in Figure 5. Figures 6 and 6a show TRC^2 as a function of film temperature; 4350 angstroms is the spectral level of irradiation.

All of the above curves, in general, show increased TRC^2 for elevated temperature. From Equation 11 differentiation with respect to time under the integral results* in

$$\frac{\dot{\sigma}}{\sigma} = \frac{-e\mu}{l} \int_0^l \int_{E_c}^{\infty} Z(E) \frac{1}{\{\exp[E + V_d(x) - E_f] / kT + 1\}^2} \frac{1}{kT} \dot{V}_d(x) dE dx \quad (12)$$

From Equation 12 it can be seen that for $E + V_d(x) > E_f$, $\frac{\dot{\sigma}}{\sigma}$ will increase with increasing temperature, if carrier equilibrium has not been reached.

*In making this differentiation under the integral, it is assumed that the integrand and its first derivative are continuous over the limits of integration.

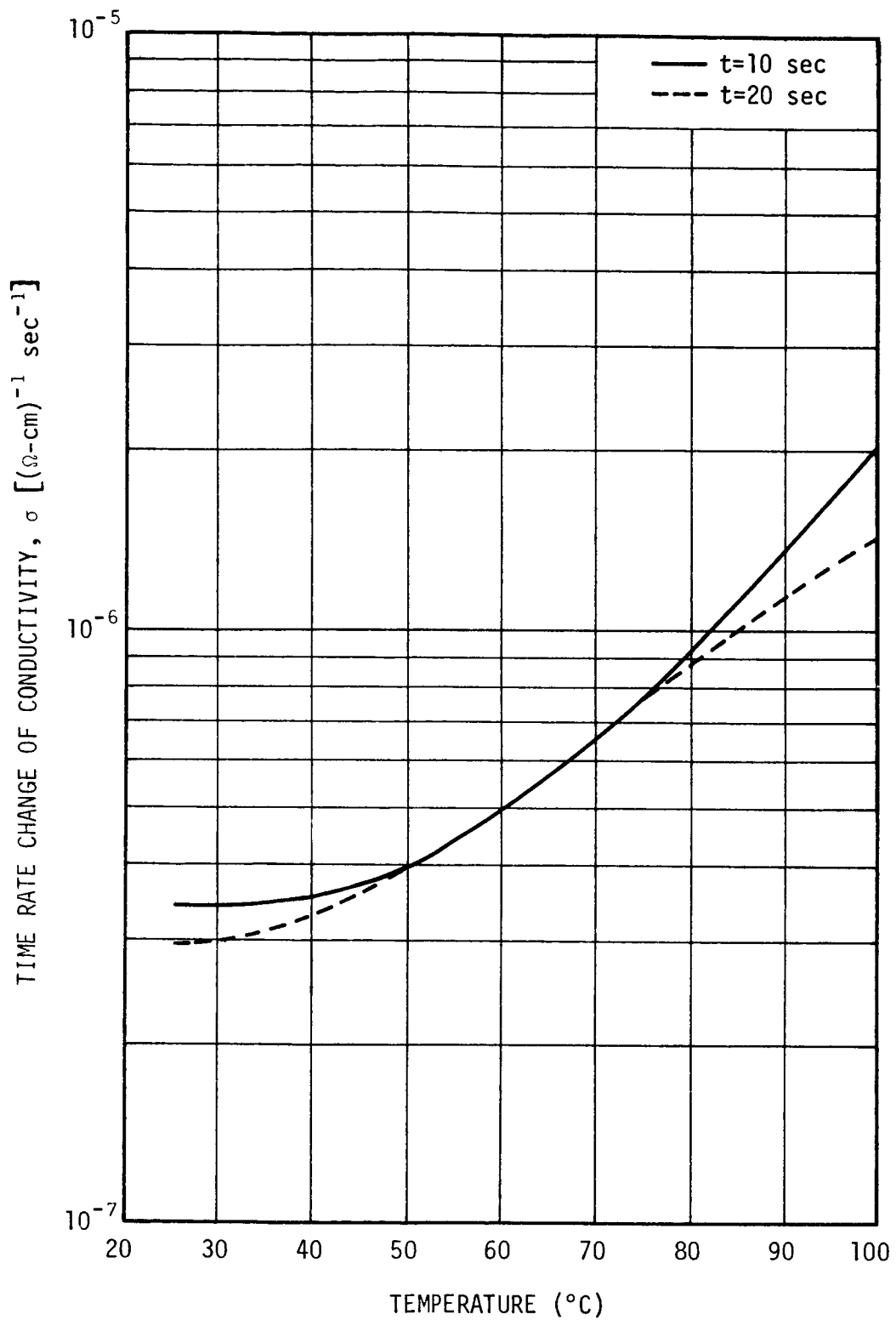


Figure 5. - Time Rate Change of Conductivity as a Function of Temperature; Degradation Phase for 3650 Å Irradiation

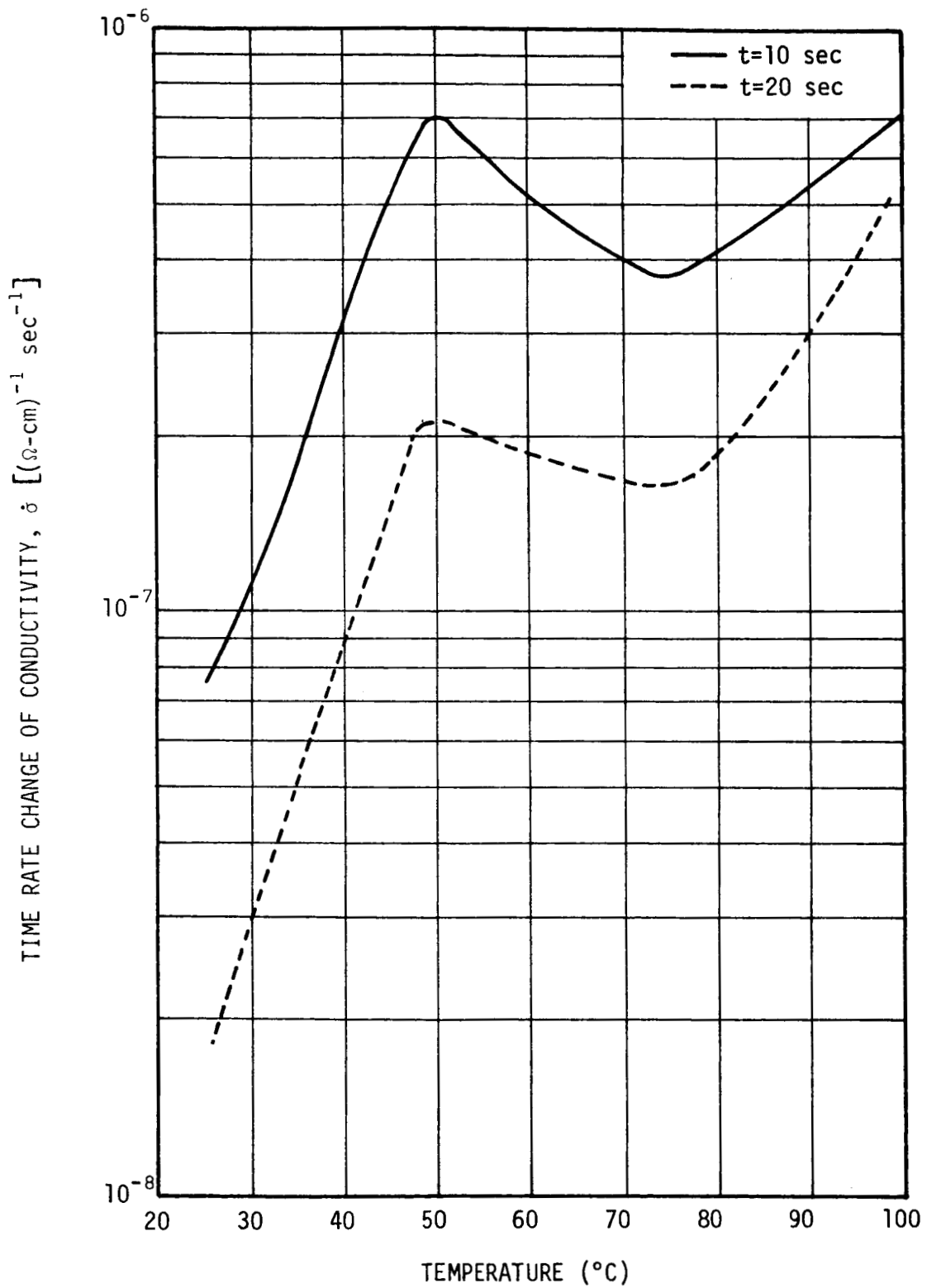


Figure 5a. - Time Rate Change of Conductivity as a Function of Temperature; Recovery Phase for 3650Å Irradiation History

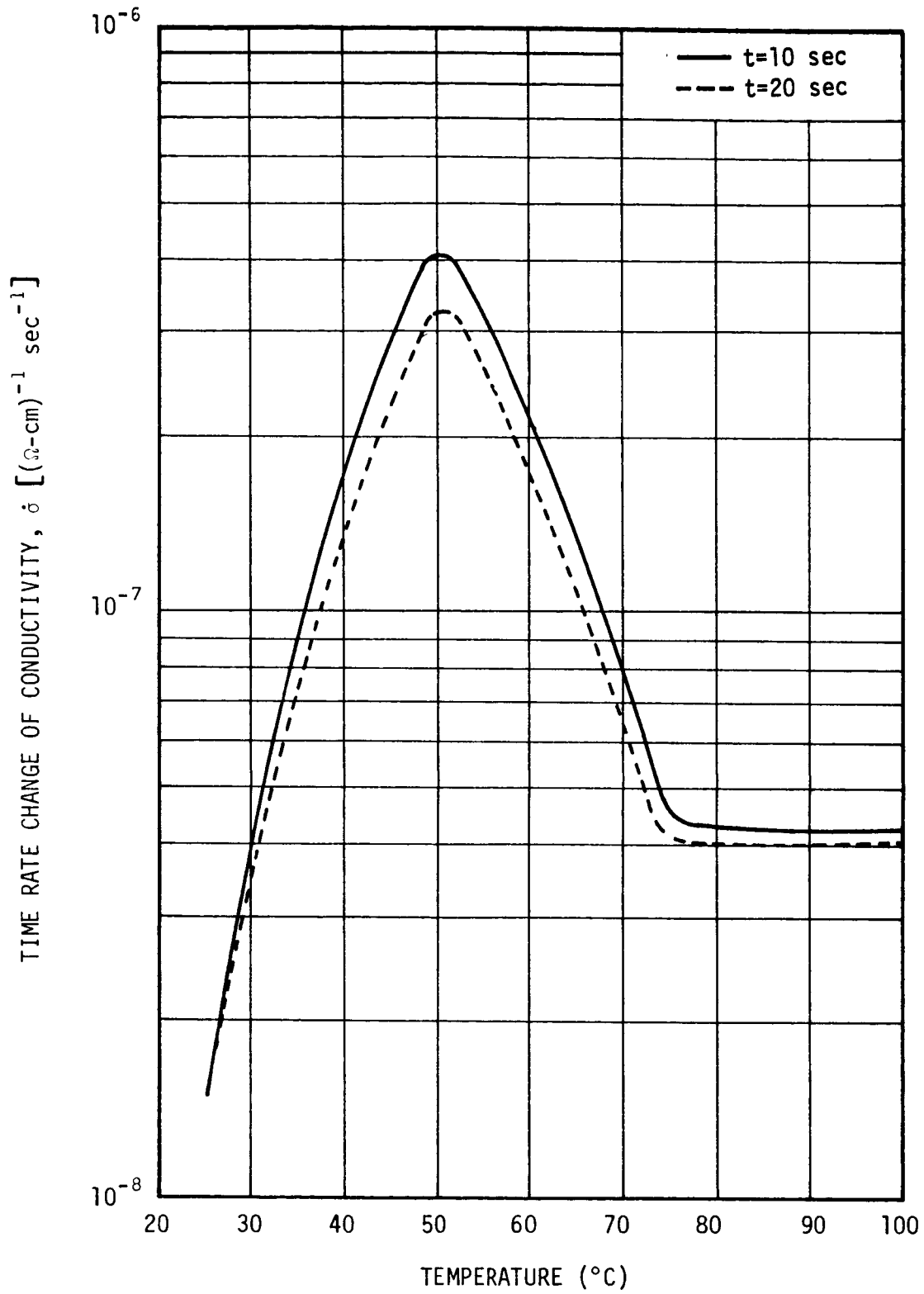


Figure 6. - Time Rate Change of Conductivity as a Function of Temperature; Degradation Phase for 4350\AA Irradiation

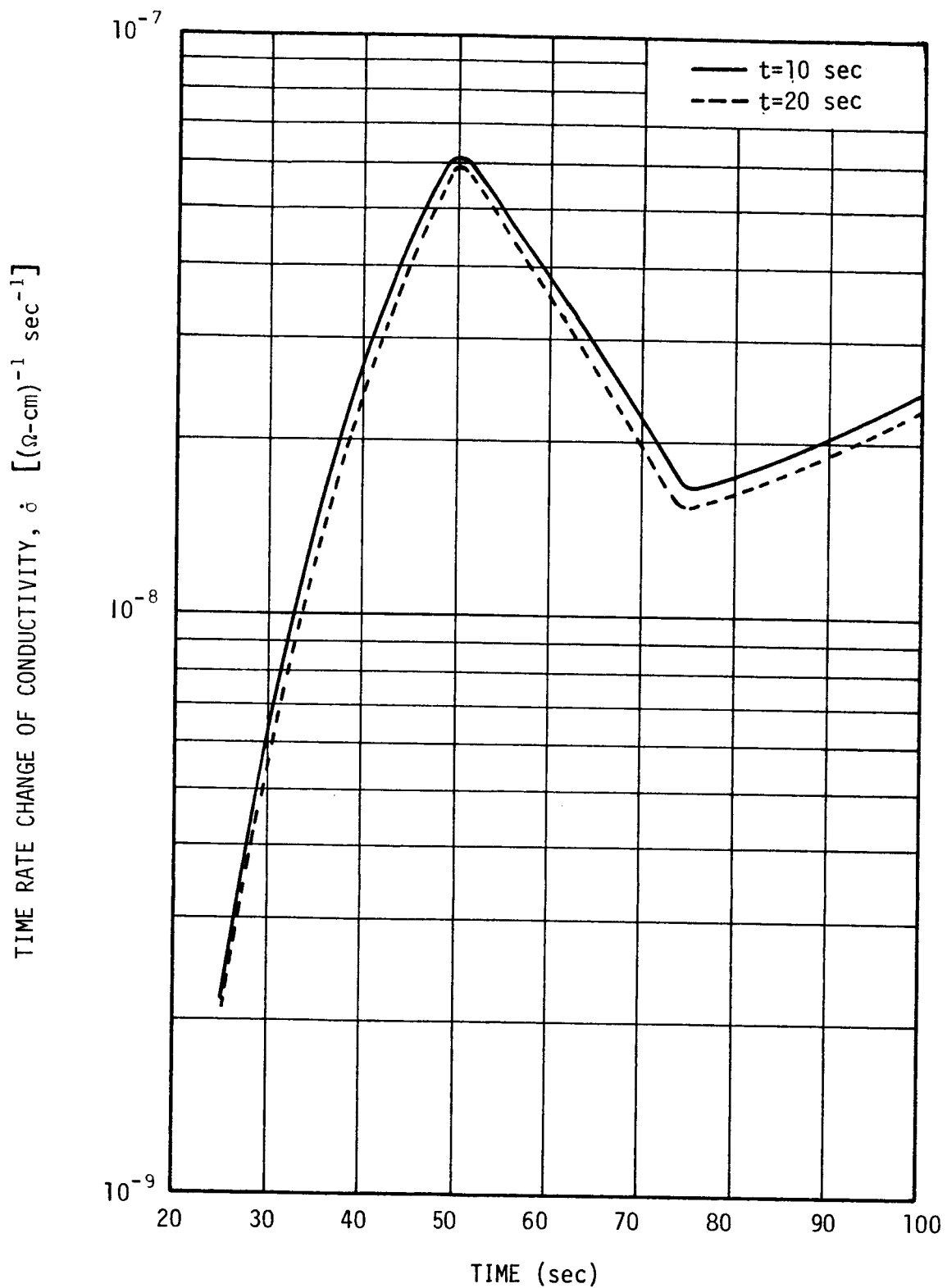


Figure 6a. - Time Rate Change of Conductivity as a Function of Temperature; Recovery Phase for 4350 Å Irradiation History

In the Figures 5, 5a, 6 and 6a only a temperature dependency trend is indicated. The temperature data was taken in increments of 25° C and hence the point density is not enough to reveal definite structure.

In Figures 5a, 6, and 6a it is seen that the rate process is reduced considerably in the 50° C to 75° C temperature range. Evidently there is a maximum in the 50° C to 75° C range and a minimum in the 50° C to 100° C range. This behavior does not have an obvious explanation; it does not arise from a change in the energy band structure of the model since the reduction of energy gap from valence or donor levels to the conduction band is monotonic with increasing temperature.⁹ The fact that in Figure 5 no such behavior is apparent is noted; however, the significance is not, at this point, understood.

A totally unsubstantiated possibility is that the TRC^2 data could result from formation of O^{--} becoming dominant in the 50° C to 100° C range. The response to 3650 angstrom irradiation might not show this effect since carriers can be excited directly to the conduction band.

It can be seen from the above figures that the slow photoresponse does occur at a rate approximately one order of magnitude greater for the 3650 angstrom irradiation when compared to the 4350 angstrom irradiation. This comparison also holds for the respective recovery rates.

The difference between the 10 and 20 second rates is only appreciable in Figure 5a. This indicates that a longer period of time is necessary to establish the dominance of the slow process when the desorption of oxygen is more complete. This is reasonable considering that donor occupation is probably reduced in the more severe degradation process.

VOLUNTARY PRESSURE RESPONSE

There is a slight change in energy structure of the ZnO model due to ambient pressure. According to Bube⁹, this relation is

$$E_G = E_G(P=0) + \gamma P \quad (13)$$

where

E_G - energy gap (eV)

γ - slope of E_G versus P (eV)

P - pressure (atm)

Gamma (γ) is on the order of one microelectron volt per atmosphere. Considering Figure 7, the magnitude change could not be attributed to the above pressure dependency. The major portion of this response is attributed to absorption of oxygen.

In Figures 8 and 9 a cursory examination of recovery of a degraded (3650 angstrom) ZnO film (730 angstrom) as a function of incremental pressure increase is given. The pressure increments cover a range of 10^{-7} torr to atmosphere. In Figure 8 it is apparent that recovery over the pressure range of 10^{-7} to 5×10^{-5} torr is negligible (aside from the normal recovery seen in high vacuum). An appreciable increase of recovery rate occurs at 1×10^{-4} torr; this is about the lower limit of molecular flow. The rate of recovery increases rapidly for higher pressures thereafter. In Figure 9, the rate process decreases with increasing pressure beyond the 50 micron level, contrary to the action in Figure 8. It might be argued that the saturation point (σ_m) is being approached, and this doubtless has some effect. However, extension of the curve at any level shows that this is not entirely the case. From this extrapolation it appears that doubling the pressure will not reduce by half the recovery time to a given recovery level. This observation, along with the observation that noticeable increase of recovery begins

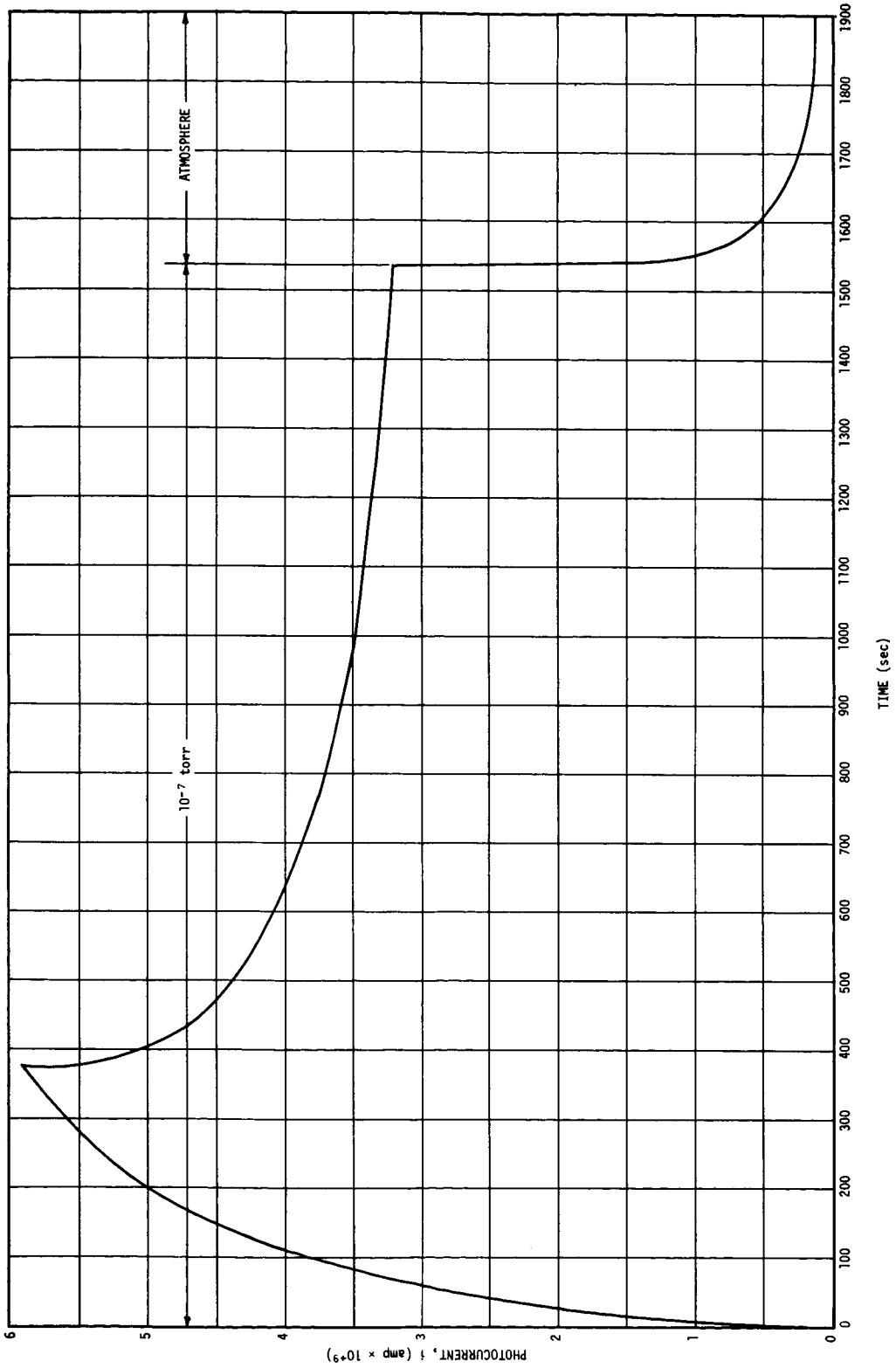


Figure 7. Recovery of ZnO as Effected by Sudden Exposure to Atmosphere

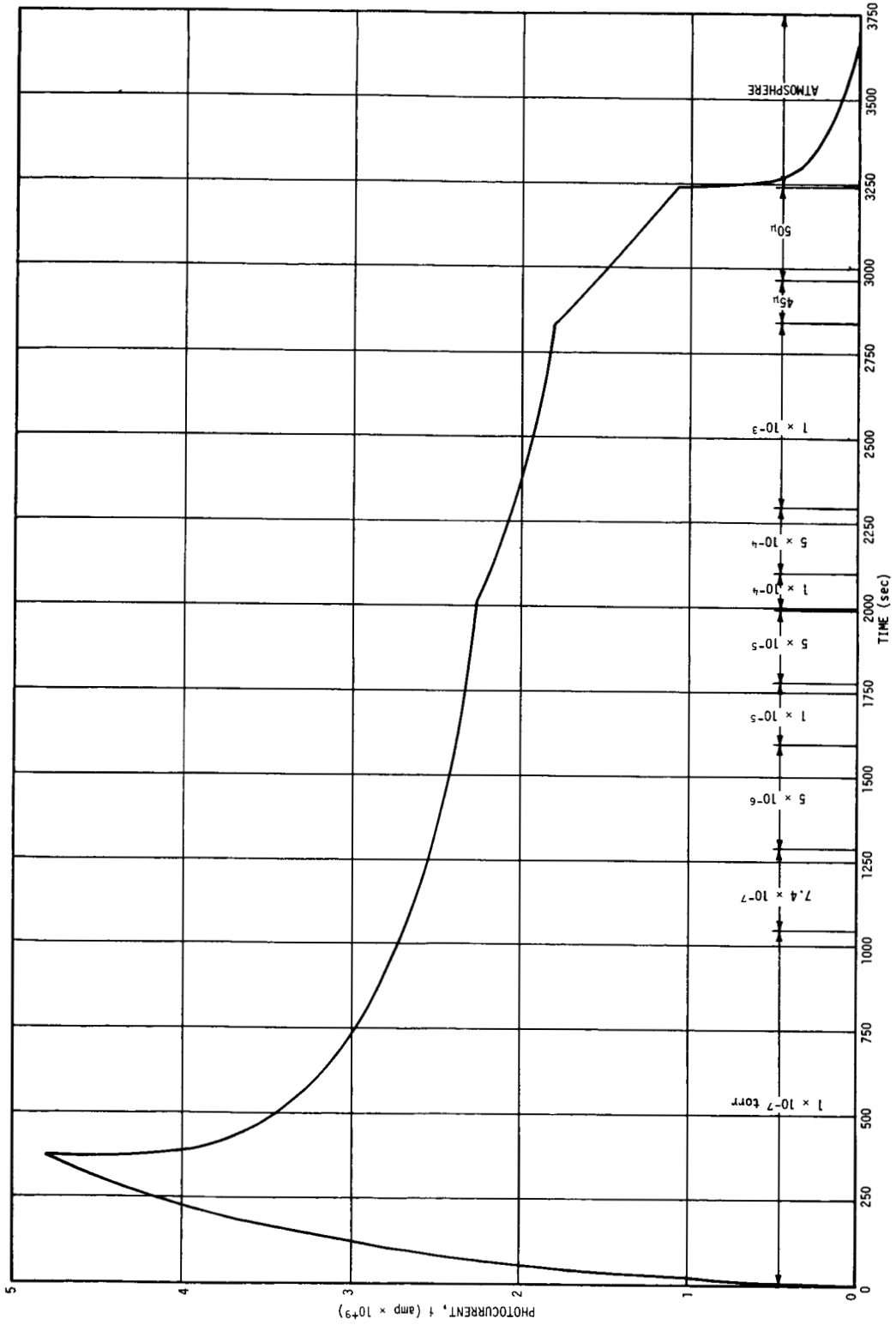


Figure 8. Film Recovery Response to Incremental Pressure Changes Over the Range of 10⁻⁷ torr to 50μ

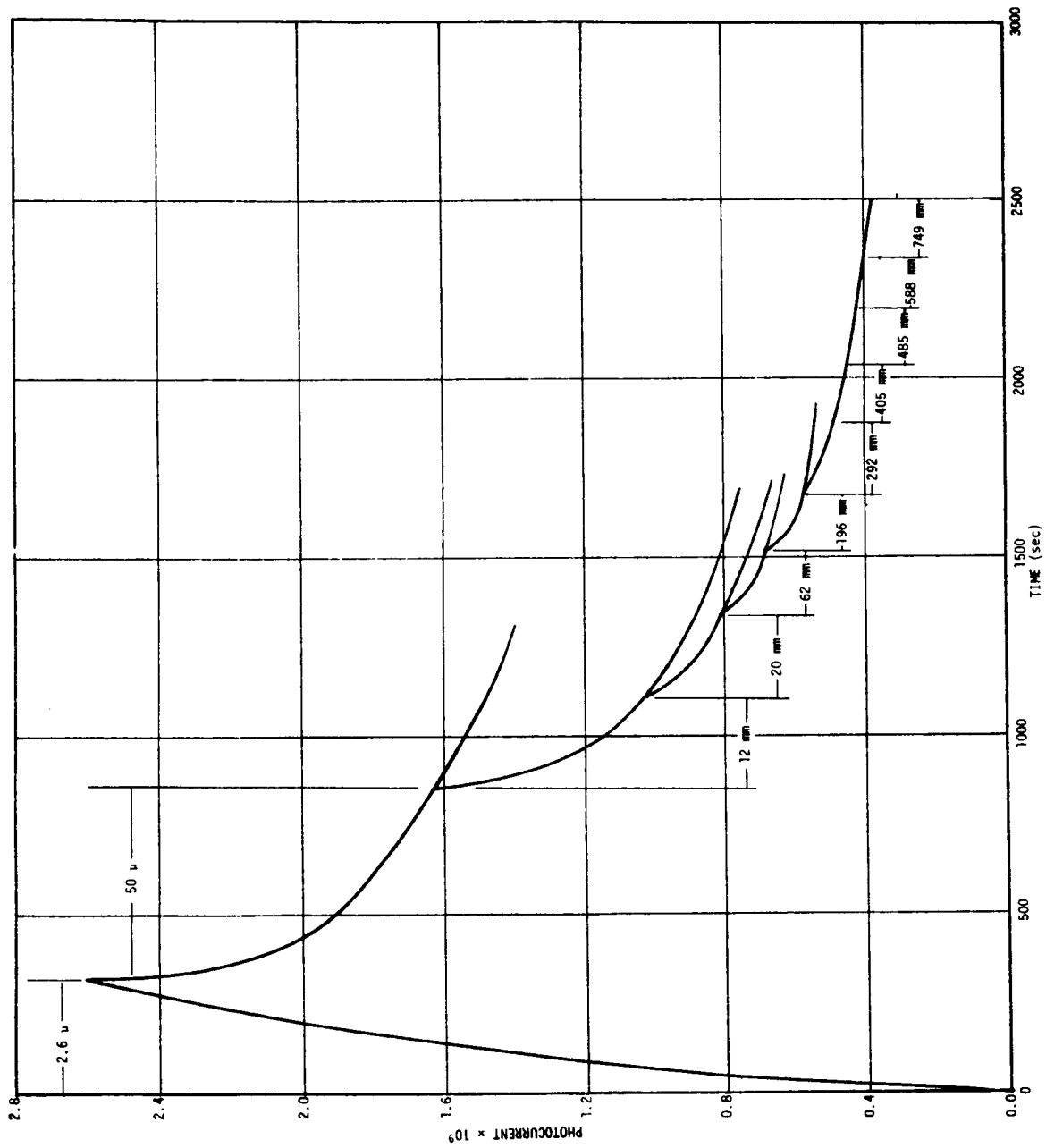


Figure 9. - Film Recovery Response to Incremental Pressure Changes Over the Range of 2.6 μ to Atmosphere

where molecular flow ends on the pressure scale, indicates a possibility that the sticking factor of oxygen to zinc oxide is not high. It evidently is important that the oxygen to be absorbed remains in the vicinity of the ZnO surface for a minimum amount of time.

CONCLUSIONS

An intrinsic parameter (conductivity) has been found to behave as an extrinsic parameter over a limited range of film thickness. A physical concept of the film structure is presented with the contention that conductivity in polycrystalline zinc oxide films is stratified. The justification for the stratification approach is given as the existence of sealed grain interfaces and the resultant decrease of the diffusion potential, $V_d(x)$, as a function of distance from the film surface.

Some observations on time rate change of conductivity and incremental pressure response are inconclusive.

REFERENCES

1. Mark, P., "RCA Review", Radio Corporation of America, pp. 461, December 1965
2. Weisz, P. B., J. Chem. Phys., 20, 1483, Sept. 1952; J. Chem. Phys., 21, 1531, September 1953
3. Hahn, E. E., J. Appl. Phys., 22, 855 (1951)
4. McDaniel, M. L., et al., "Hall and Photoresponse Measurements Associated with Ultraviolet and Near Ultraviolet Degradation of Thin Zinc Oxide Films", Brown Engineering Company, Inc., Technical Note R-229, May 1967
5. Harrison, S. E., Phys. Rev., 93, 52 (1953)
6. Heiland, G., Disc. Faraday Soc., 28, 168-182 (1959)
7. van der Ziel, A., Solid State Physical Electronics, Prentice-Hall, Englewood Cliffs, N. J., pp. 241-253, 1957
8. Leonard, W. F., and R. L. Ramey, J. Appl. Phys., 35, 2963, (1964)
9. Bube, R. H., Photoconductivity of Solids, John Wiley & Sons, 1960