JOURNAL OF CATALYSIS 4, 415–429 (1965)

A Kinetic Study of the Slow Rise and Decay of the Photoconductivity in Zinc Oxide

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Received May 5, 1964

The kinetics of the slow rise and decay of the photoconductivity in sintered specimens of pure ZnO has been studied under different experimental conditions. The samples have been submitted to pretreatments in oxiding as well as in reducing atmospheres. The kinetics has been studied at oxygen pressures between 10^{-6} and 150 Torr and at temperature between 25° and 400°C. It is shown that at temperatures below 100°C and above 300°C the kinetics of both the rise and the decay can be approximated by the equation: $\Delta x = (2.3/\alpha) \log (t + t_0) + (2.3/\alpha) \log a\alpha$. The values of the parameters of this equation are found to depend on the experimental conditions.

In the temperature range 100–300°C the behavior is complex.

The correlation with previously observed photoadsorption and photodesorption effects is discussed as well as the role of different types of oxygen chemisorption.

To interpret present and previous results it is necessary to postulate that two different mechanisms are responsible for the different behavior observed on reduced and on oxidized samples. The two mechanisms are characterized by their different spectral sensitivity and by their dependence on the concentration of adsorbed oxygen.

Irradiation of zinc oxide surfaces with light, γ rays, or electrons causes a variation of the electrical conductivity of the oxide. In favorable cases it is possible to observe both a fast and a slow process (*1*). The fast process corresponds to an increase of the conductivity under irradiation until a saturation value is reached in times of the order of a second or less. A correspondingly rapid decay of the conductivity to the initial value is observed when irradiation is discontinued.

The slow process corresponds to a rise of the conductivity which leads to saturation values in times which range from a few minutes to many hours, according to the experimental conditions. The decay in the dark is correspondingly slow. A slow decrease of the conductivity under irradiation has also been reported (*1*, *2*). While the fast process is likely to correspond to purely electronic phenomena, the slow process has been associated with a slow desorption or adsorption of oxygen under the action of radiation (*1*, *3*). The interpretation of the slow rise and decay of the photoconductivity as an oxygen adsorption process has been supported by independent observations which showed that the conductivity increase under irradiation is accompanied by desorption of oxygen (*4*), which was also detected manometrically (*5*). Other investigations have shown that it is possible to observe both a desorption or an adsorption of oxygen under irradiation depending on the temperature, the oxygen pressure, and the defective state of the surface (*6–11*).

A theoretical interpretation of the photoadsorption and photodesorption effects has been given by Volkenstein (*12*). On the basis of the above-mentioned results one would therefore expect to observe a decrease of the conductivity under illumination when experimental conditions are similar to those leading to photoadsorption. However, this expectation was not confirmed by previous work from this laboratory (*13*) which showed that the observed conductivity increase should be attributed to desorption of small amounts of oxygen strongly bound to the surface or to the direct photolysis of the surface layers, as suggested by previous investigations on single crystals (*14*). Similar conclusions were independently reached by others (*10*) in a study of the behavior of ZnO under γ irradiation.

At present, although there seems to be little doubt that the slow rise and decay of the photoconductivity are associated with a modification of the adsorption equilibrium of oxygen, the correlation between the observed photoadsorption and photodesorption effects and the photoconductivity process has not been established with any certainty and requires further study. In the present paper the kinetics of the slow rise and decay of the conductivity has been investigated on pure ZnO. Prior to illumination the samples have been submitted to treatments in oxidizing and reducing atmospheres. The kinetics has been studied at oxygen pressures between 10^{-6} and 150 Torr and at temperatures between 25° and 400°C.

Experimental Methods

The sample to be irradiated was placed inside a cylindrical silica cell, about 3 cm in diameter, with a flat optical window at the bottom. The cell was connected to the high-vacuum system, to gas reservoirs, mercury manometers, and Pirani and Philips gauges. This cell could fit vertically into the hole of a mobile furnace. The temperature was kept constant by means of a thermoregulator and was read by means of a thermocouple held against the sample. The samples consisted of sintered pellets (see below) 1 cm in diameter and 1–2 mm thick. One side of the pellet was coated with an evaporated film of gold in such a way as to leave a noncoated gap of about 4 mm in the center. The pellet was clamped to stainless steel electrodes, the electric contact being established between the electrodes and the gold film. The pellet was hung in the center of the cell and illuminated from the bottom so that only the noncoated gap was illuminated.

The light source was a UV mercury lamp (Hanau Q 81) placed in a cooling housing provided with an aluminum reflector and a shutter. During illumination no temperature rise could be detected by the thermocouple placed against the sample ($\Delta T < 0.1$°C) if a sufficiently strong air blast was maintained between the lamp and the bottom of the furnace. The light was shone on the samples either unfiltered or filtered through Wratten Filters (Kodak 2B and 47) or through an UV interference filter (Schott 6600–08, named Filter 368 in the text). From the spectral distribution of the intensity of the UV lamp and from the characteristics of the filters, as given by the manufacturers, one can calculate that Filter 2B transmits more than 1% at wavelengths longer than about 390 mμ. The intensity (photons/cm^2 sec) of the light transmitted through this filter corresponds to approximately 65% of the intensity of the unfiltered radiation in the spectral region of transparency of the filter, and to about 20% of the total intensity from the lamp. Filter 47 transmits more than 1% between 380 and 530 mμ. The corresponding intensities of the transmitted light are 35% and 10%. Filter 368 transmits light of wavelength 368 ± 9 mμ, and the intensity of the transmitted light is about 15% of the total UV intensity and about 10% of the total intensity.

Conductivities in the range 10^{-1}–10^{-10} mho were measured by means of an AC bridge (Wayne Kerr B221) operating at 1592 cycles/sec.

Pure ZnO was obtained from high-purity ZnC_2O_4 by thermal decomposition in air at 450°C, pressing at 5 t/cm^2 and sintering at 900°C for 5 hr in air.

The kinetics of the conductivity change was followed either on fresh samples, i.e. on samples which did not undergo any preliminary surface treatment or on samples pretreated according to the following procedures:

(1) Treatment at 450°C at an oxygen pressure of 10^{-6} Torr for 4 hr and successive cooling in high vacuum to the temperature of the experiment.

(2) After treatment (1) hydrogen was admitted at 100 Torr and 400°C and kept in contact with the sample for 30 min. The

sample was successively cooled in hydrogen to the desired temperature and evacuated at this temperature.

(3) Like treatment (2), but with admission of 1 Torr of hydrogen at 520°C for 5 min.

(4) After treatment (1) oxygen was admitted at 400°C at a pressure of 100 Torr and kept in contact with the sample for 60 min. The sample was successively cooled in oxygen to the temperature of the experiment.

Experimental Results

Measurements at Room Temperature

Two typical rise and decay curves determined after various pretreatments and different oxygen pressures are given in Fig. 1.

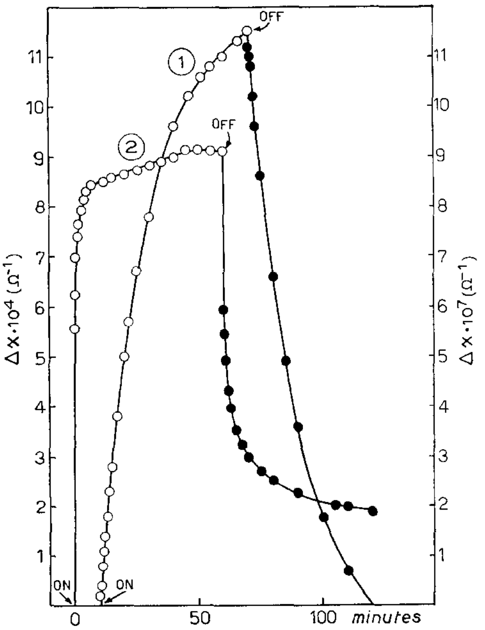

FIG. 1. The conductivity change as a function of time for a ZnO sample irradiated with the unfiltered radiation at 25°C. Curve 1 (left scale)—sample pretreated in high vacuum at 450°C irradiated at 10^{-6} Torr. Curve 2 (right scale)—fresh sample irradiated at 10^2 Torr.

As will become apparent from the presentation of the data it is possible to approximate the kinetics of both the slow rise and the slow decay by means of the differential equation

$$d\Delta x/dt = a \exp(-\alpha \Delta x) \qquad \text{(1a)}$$

which integrates to

$$\Delta x = (2.3/\alpha) \log (t + t_0) + (2.3/\alpha) \log a\alpha \qquad \text{(1b)}$$

For the conductivity rise $\Delta x = x_t - x_i$ and for the decay $\Delta x = x_f - x_t$; x_t is the conductivity measured at time t, x_i the initial conductivity in the dark, and x_f is the final value of the conductivity measured immediately before the illumination was discontinued. Linearization of Δx-log $(t + t_0)$ plots has been found to be possible in all cases by a suitable choice of the parameter t_0 which was determined by trial and error.

In some cases the linear plots extrapolate, at time $t = 0$, to a value $\Delta x > 0$. The value of Δx extrapolated at $t = 0$ will be designated by Δx_0. From the linear plots one determines the value of α and from the relationship $t_0 = 1/\alpha a$, which is valid when $\Delta x_0 = 0$, one determines the value of the initial rate a. When $\Delta x_0 > 0$, t_0 is given by $1/a^*\alpha$ where $a^* \neq a$ (*15*).

The kinetics of the photoconductivity rise and decay has been studied both in the presence and in the absence of selected light filters. Typical rise and decay curves determined either on fresh samples or after various pretreatments, using the unfiltered radiation, have been plotted in Fig. 2 according to Eq. (1b). The kinetics observed in the presence or in the absence of filters have been compared in Fig. 3 for various experimental conditions. The dependence on the oxygen pressure of the conductivity increase Δx_{60} determined after 60 min of irradiation is given in Fig. 4 for Sample No. 4. The ratio between the conductivity increase observed after 60 min in the presence of Filter 2B ($\Delta x_{60}{}^F$) and Δx_{60} has been plotted as a function of oxygen pressure in Fig. 5. In Fig. 6 the conductivity increases observed in the presence of Filters 47 and 368 have been compared. Figure 7 gives the pressure dependence of the parameter α and Fig. 8 gives the dependence on the pressure of either a or a^*.

In Tables 1 and 2 the ratio between the

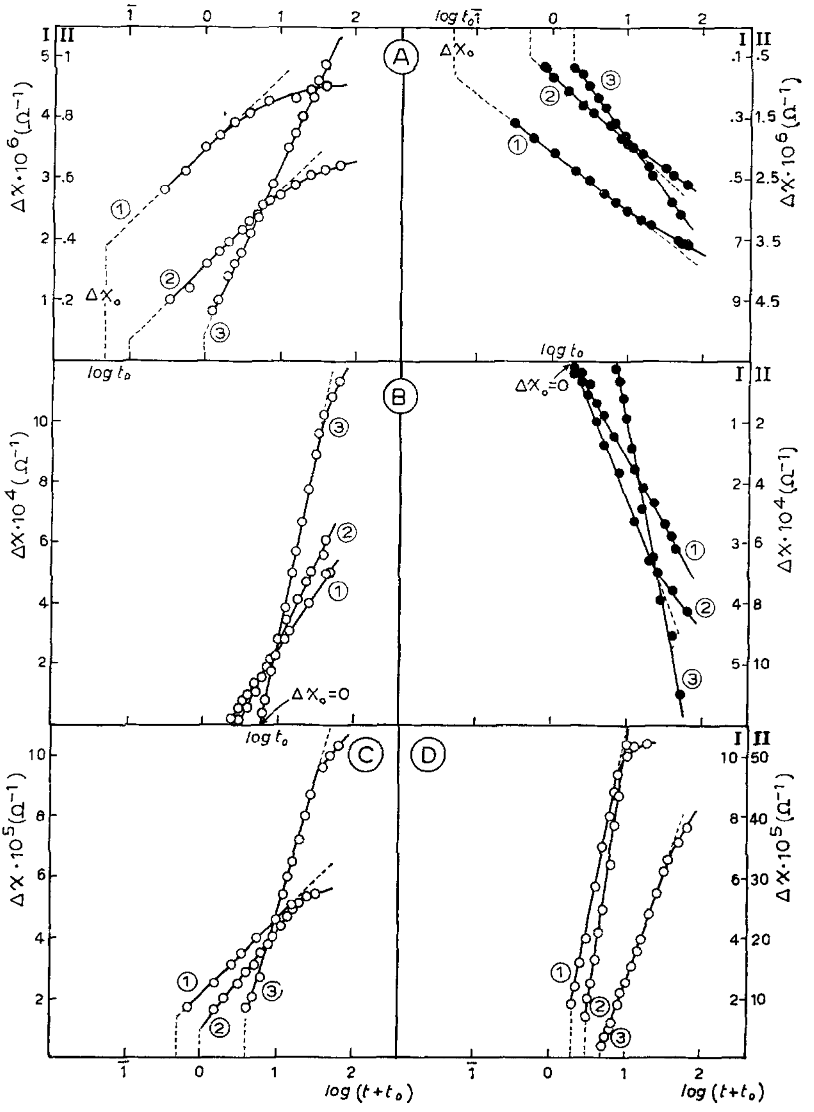

FIG. 2. Plots of the conductivity change as a function of log $(t + t_0)$ for samples irradiated with the unfiltered radiation at 25° at different oxygen pressures. (A) Sample No. 6, fresh sample. *Left:* conductivity rise; Curves 1, 2 (Scale II), $P_{O_2} = 10^2$, 10^{-2} Torr; Curve 3 (Scale I), $P_{O_2} = 10^{-6}$ Torr. *Right:* conductivity decay; Curves 1, 2 (Scale I), $P_{O_2} = 10^2$, 10^{-2} Torr; Curve 3, $P_{O_2} = 10^{-6}$ Torr. (B) Sample No. 6, pretreated in high vacuum at 450°C. *Left:* conductivity rise; Curves 1, 2, 3: $P_{O_2} = 10^2$, 10^{-2}, 10^{-6} Torr. *Right:* conductivity decay; Curves 1, 2 (Scale I); Curve 3 (Scale II). (C) Sample No. 4, pretreated in O_2 at 400°C; conductivity rise; Curves 1, 2, 3: $P_{O_2} = 10^2$, 10^{-2}, 10^{-6} Torr. (D) Sample No. 4, pretreated in H_2 at 400°C; conductivity rise, Curves 1, 2, 3; $P_{O_2} = 10^2$, 10^{-2}, 10^{-6} Torr.

Δx_0 values determined for the rise (Δx_0^R) or the decay (Δx_0^D) and the corresponding value of Δx_{60} is given for different experimental conditions. The tables also include the per cent decay in the dark observed after 60 min, the values of t_0 for the rise (t_0^R) and the decay (t_0^D), and the values of t_b^R and t_b^D where t_b is the time at which a break is first observed in the linear Δx–log $(t + t_0)$ plots.

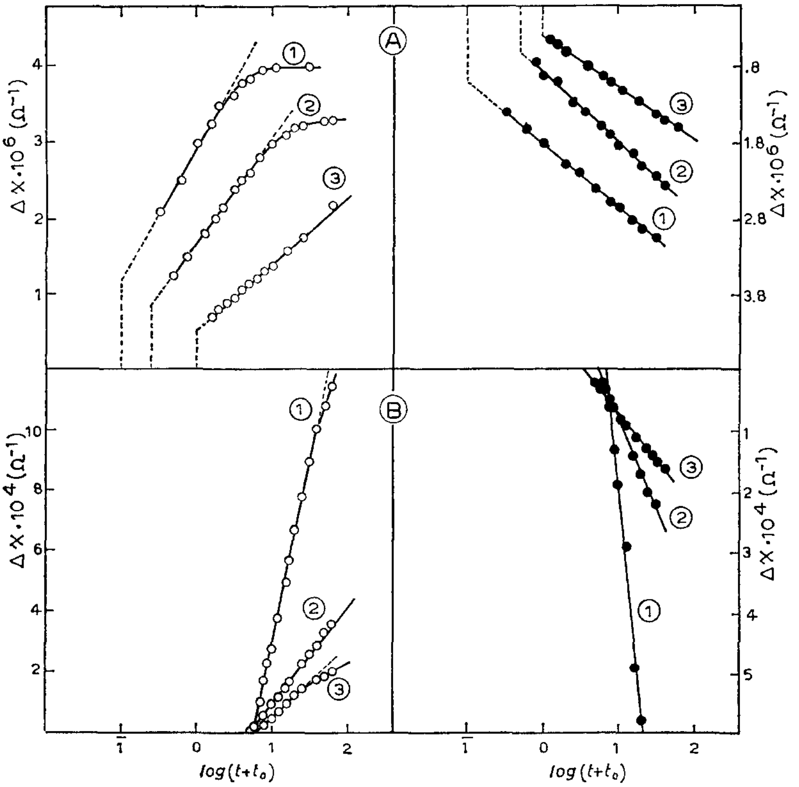

FIG. 3. Plots of the conductivity change as a function of log $(t + t_0)$ for sample No. 6, irradiated at 25°C in the presence of different light filters. (A) Fresh sample irradiated at 10^2 Torr. *Left:* conductivity rise; Curves 1, 2, 3: unfiltered radiation, Filter 2B, Filter 47. *Right:* conductivity decay. (B) Sample pretreated in high vacuum at 450°C irradiated at 10^{-6} Torr. *Left:* conductivity rise; Curves 1, 2, 3: unfiltered radiation, Filter 2B, Filter 47. *Right:* conductivity decay.

Figure 9 illustrates the following experiments: A given conductivity increase Δx was reached with the use of either Filter 47, Filter 2B, or with the unfiltered radiation, in correspondingly shorter times. Illumination was thereafter discontinued and the decay kinetics followed in the usual way. The various decay kinetics have been plotted in the figure also according to Eq. (1). The behavior of oxidized samples (Fig. 9A) confirms previous results (*3*).

Measurements above Room Temperature

The results obtained at different temperatures with a fresh sample at 150 Torr are illustrated in Fig. 10. One appreciates that in the temperature region between approximately 100° and 300°C, if use is made of the unfiltered radiation, the kinetics of both the rise and the decay are complex. Above about 300°C illumination causes a definite decrease of the conductivity which reverts to its initial value when irradiation is discontinued. The rate at which the initial conductivity is reached in the dark increases with increasing temperature. At these temperatures the decay kinetics under illumination and the kinetics of the conductivity rise in the dark can be approximated by Eq. 1(b), at least after a short initial period. The patterns of behavior illustrated in Fig. 10 can be reproduced on the same sample under identical conditions. However, Fig. 11 shows that the behavior observed at about 200°C and 150 Torr on differently oxidized samples can be quite different. To elucidate

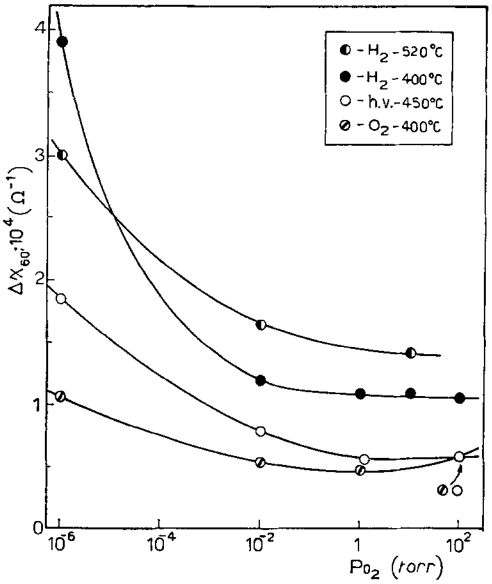

Fig. 4. A plot of the conductivity rise measured at 25°C after 60 min of irradiation with the unfiltered radiation (Δx_{60}) as a function of the oxygen pressure. Sample No. 4 pretreated under different conditions.

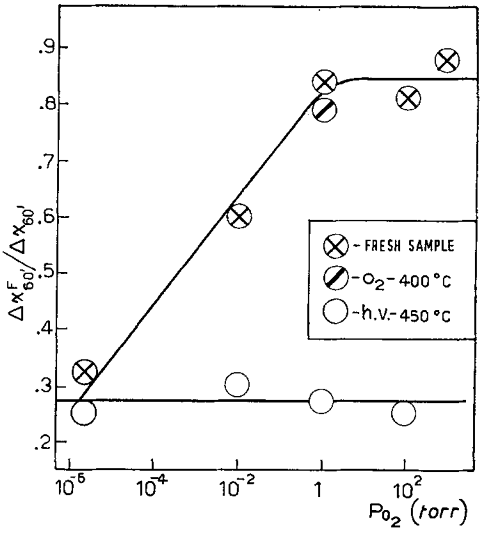

Fig. 5. A plot of the ratio between the conductivity rise measured at 25° after 60 min of irradiation in the presence of Filter 2B (Δx^F_{60}) and the corresponding rise with the unfiltered radiation (Δx_{60}), as a function of the oxygen pressure.

TABLE 1

ZnO—Sample No. 6

Filter	P_{O_2} (Torr)	$\frac{\Delta x_0^R}{\Delta x_{60}} 100$	$\frac{\Delta x_0^D}{\Delta x_{60}} 100$	% Decay after 60 min	t_0^R (min)	t_0^D (min)	t_b^R (min)	t_b^D (min)
				Fresh sample				
Unf.	7.6 10^2	42	22	76	0.05	0.1	2.5	10
2B		24	15	64	0.05	0.25	2.5	60
Unf.	10^2	40	18	79	0.05	0.05	2.5	9
2B		19	15	80	0.05	0.25	2.5	>60
Unf.	1	38	21	85	0.05	0.1	3.5	12
2B		15	17	75	0.05	0.5	6.5	60
Unf.	10^{-2}	9	8	81	0.1	0.5	8.5	15
2B		19	14	63	0.25	1	25	40
Unf.	10^{-6}	8	11	96	1	2	>60	>60
2B		16	17	60	9	2	>60	>60
				High vacuum, 450°C				
Unf.	10^2	0	0	90	2	2	>60	45
2B		0	0	77	0.5	1	15	8
Unf.	1	0	0	73	4	3	>60	20
2B		0	0	64	0.5	2	>60	10
Unf.	10^{-2}	0	0	63	3	2	>60	20
2B		0	0	—	4	—	>60	—
Unf.	10^{-6}	0	0	100	6	7	40	>60
2B		0	0	80	5	6	>60	>26

TABLE 2
ZnO—SAMPLE No. 4

P_{O_2} (Torr)	$\frac{\Delta x_0^R}{\Delta x_{60}}100$	$\frac{\Delta x_0^D}{\Delta x_{60}}100$	% Decay after 60 min	t_0^R (min)	t_0^D (min)	t_b^R (min)	t_b^D (min)
			H_2, 520°C				
10^{-2}	9	2	100	3	2	>5	>15
10^{-6}	6	0	100	5	5	25	>40
			H_2, 400°C				
1	13	6	100	2	2	13	25
10^{-2}	10	0	100	3	2	10	>20
10^{-6}	4	1	100	5	5	30	30
			O_2, 400°C				
10^2	21	—	—	0.5	—	15	—
1	15	—	—	0.5	—	15	—
10^{-6}	11	—	—	4	—	25	—

the complex behavior observed between 100° and 300°C the experiments illustrated in Fig. 12 have been performed. A sample pretreated in high vacuum at 450° was treated with 230 Torr of oxygen at 400° for 145 min. Illumination of this sample at 243°C with the unfiltered radiation gives curve 1 of Fig. 12A, while irradiation with filter 368 gives curve 2. The same sample was again treated in high vacuum at 450° and kept in contact with 60 Torr of oxygen at 400° for 10 min. The behavior observed at 154°C with the use of the unfiltered radiation is represented by curve 1 of Fig. 12B; curve 2 represents the behavior observed when light was filtered through Filter 2B.

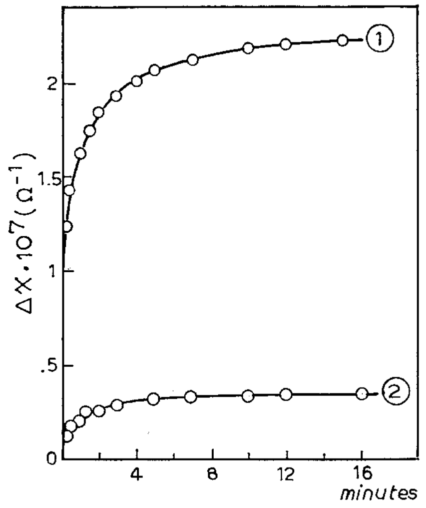

FIG. 6. A plot of the conductivity change as a function of time for sample No. 6 pretreated in O_2 at 400°C and irradiated at 25°C at 230 Torr. Curve 1, Filter 47; Curve 2, Filter 368.

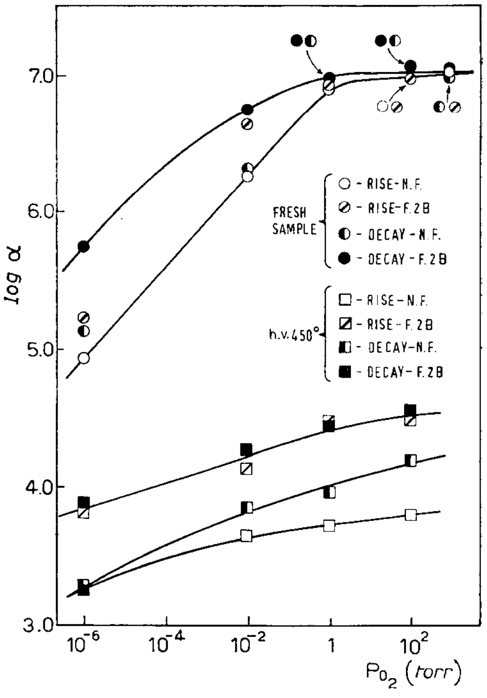

FIG. 7. A plot of log α as a function of the oxygen pressure; Sample No. 6, 25°C.

Pretreatment in high vacuum at 450° modifies the behavior of these samples in that one can only observe a conductivity increases under illumination at all the temperatures investigated. The values of Δx_{60} observed at different temperatures under various oxygen pressures have been plotted in Fig. 13.

DISCUSSION

Photoadsorption, Photodesorption, and Photoconductivity

Irradiation of a ZnO surface with light, γ rays, or electrons entrains, as already mentioned in the introduction, either adsorption or desorption of oxygen according to the temperature, the pressure, and the defective state of the surface. The results obtained by

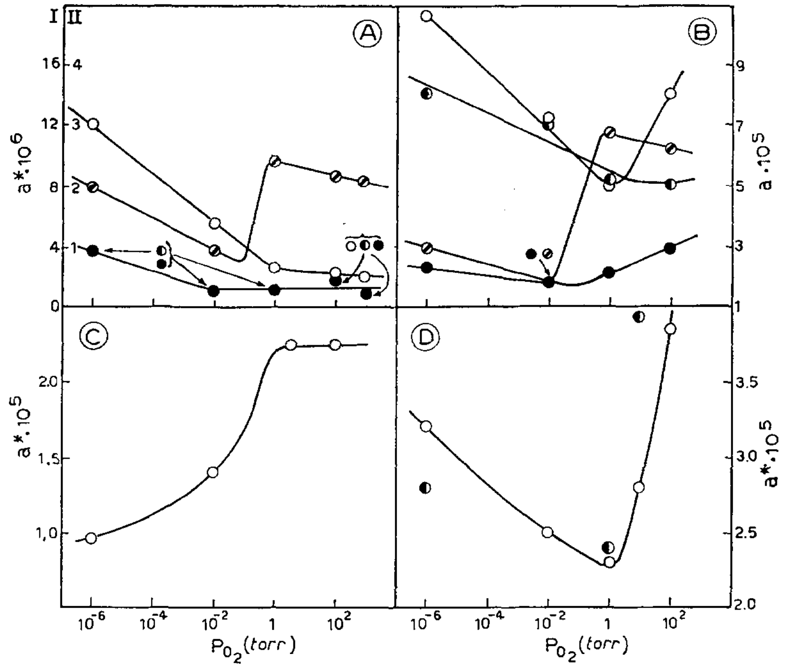

FIG. 8. Plots of a or a^* as a function of the oxygen pressure; ○, ◐, conductivity rise and decay with the unfiltered radiation; ⊘, ●, conductivity rise and decay in the presence of Filter 2B (25°C). Pretreatment: (A) Sample No. 6, fresh sample; Scale I, unfiltered radiation; Scale II, Filter 2B. (B) Sample No. 6, high vacuum, 450°C. (C) Sample No. 4, O_2, 400°C. (D) Sample No. 4, H_2, 400°C.

different authors (*6–11*), can be summarized as follows: According to the data of ref. (*7*) an *increase* in the concentration of excess zinc, causes a reversal of the photoeffect from photodesorption to photoadsorption. The opposite trend is observed according to the data of refs. (*6*, *9*, *11*). Photoadsorption was in fact observed on the more oxidized surfaces. On oxidized samples at room temperature one observes a change from photodesorption to photoadsorption by decreasing the pressure, while at 400°C this trend is reversed (*8*).

The theoretical treatment of photoadsorption effects given by Volkenstein (*12*) qualitatively accounts for the observed behavior. According to Volkenstein, the sign of the photoeffect [(+) photoadsorption, (−) photodesorption] is determined by the sign of $\varphi = \epsilon + V_0 - v$; ϵ gives the position of the Fermi level of the semiconductor with respect to the center of the forbidden gap, V_0 is the voltage drop across the barrier layer on the surface, and v gives the position of the acceptor level corresponding to the adsorbed molecule or atom. The theory shows that the sign of φ, hence the sign of the photoeffect, changes twice when plotted as a function of the concentration of excess zinc. This provides a qualitative explanation of the opposite trends observed by different authors [see Fig. 3 of ref. (*12*c)].

The reversal of the sign of the photoeffect at different pressures is also accounted for by this theory and is attributed to an increase of V_0 with increasing pressure at 25°C and to a decrease of ϵ with increasing pressure at 400°C [see Fig. 2 of ref. (*12*c)].

On the basis of the positive and negative photoeffects which have been observed for oxygen chemisorption one would have expected to find an at least qualitative correlation between the conductivity *rise* under illumination and photo*desorption* and between the *decay* of the conductivity under irradiation and photo*adsorption*.

The present results show that such a

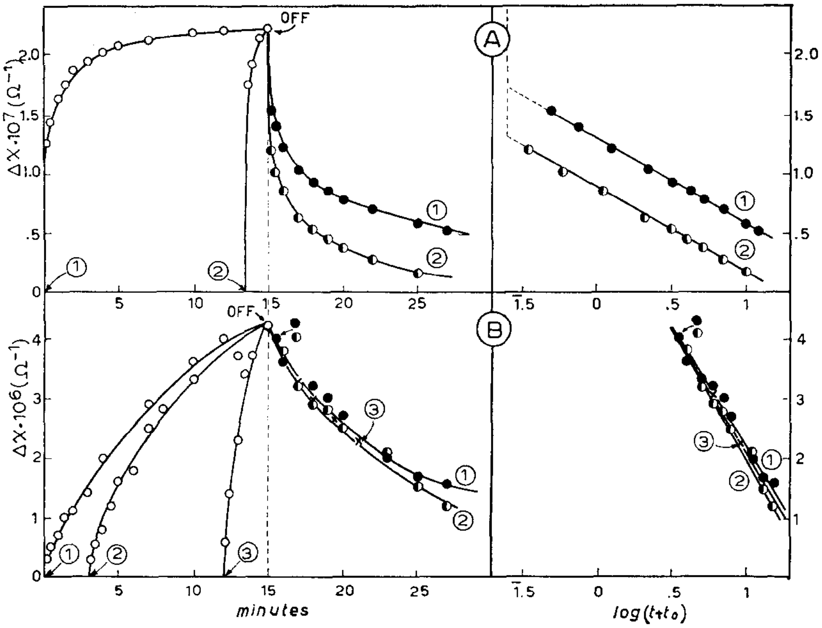

FIG. 9. (A) *Left:* Conductivity change as a function of time for Sample No. 6 pretreated in O_2 at 400°C, irradiated at 25°C at 10^2 Torr in the presence of filters. Curve 1, Filter 47; Curve 2, Filter 2B. *Right:* decay curves plotted according to Eq. (1). (B) Same sample pretreated in high vacuum at 450° irradiated at 25°C at 10^{-6} Torr. *Left:* Curve 1, Filter 47; Curve 2, Filter 2B; Curve 3, unfiltered radiation. *Right:* decay curves plotted according to Eq. (1).

correlation seems to exist only above about 300°C.

As clearly indicated by Fig. 10 oxidized samples irradiated at temperatures above 300°C under 150 Torr of oxygen show a decrease of the conductivity under illumination. The conductivity reverts to the initial value, more or less rapidly according to temperature. Samples pretreated in high vacuum at 450°C and irradiated at pressures up to 10 Torr show an increase of the conductivity under illumination at all the temperatures investigated (Fig. 13). The results obtained above 300°C do correspond therefore to the predictions of Volkenstein's theory and to the experimental findings of Romero-Rossi and Stone (*8*) at 400°C.

In fact one observes a decrease of the conductivity (photoadsorption) under illumination on oxidized surfaces (fresh samples) at high pressure, while the conductivity increases (photodesorption) under irradiation on the more reduced surfaces obtained by treatment in high vacuum at 450°C.

The behavior in the temperature interval between about 100° and 300°C is complex and will further be examined in the course of the present discussion.

According to the present data the behavior at room temperature always corresponds to an increase of the conductivity under illumination. In view of the wide range of pressures, initial conductivities, and pretreatments, one would have expected to observe an increase or a decrease of the conductivity under illumination according to whether the experimental conditions correspond to those leading to photodesorption or to photoadsorption.

At room temperature there is apparently no correlation between the measured photoconductivity and the photoeffects observed for oxygen chemisorption.

The expectation that such a correlation exists is, however, based on the assumption that oxygen adsorbed or desorbed in amounts sufficiently large to be detected manometrically is also responsible for the observed conductivity changes. This was in fact the

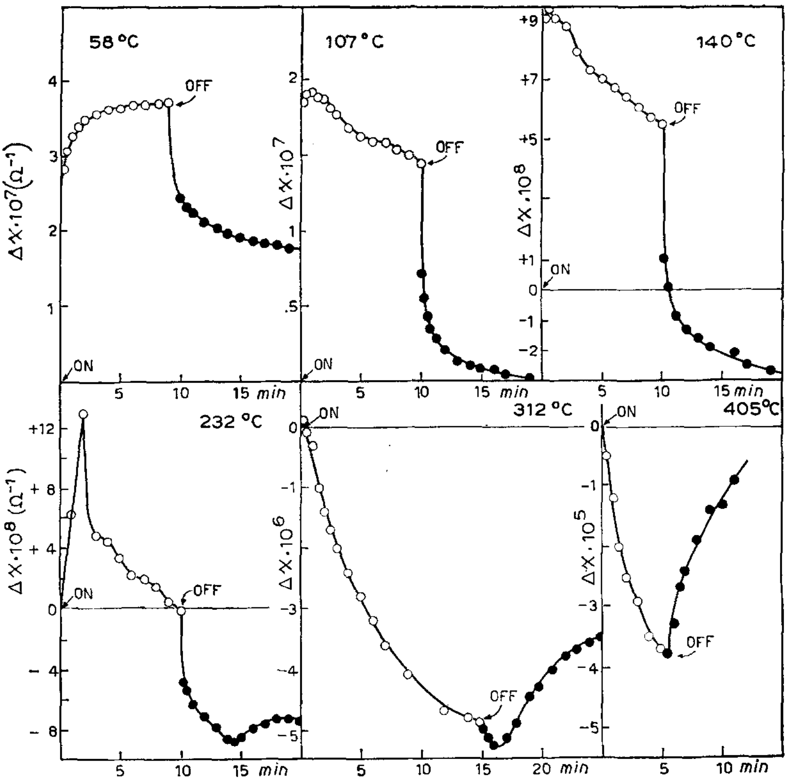

FIG. 10. Conductivity rise and decay curves at different temperatures determined on a fresh sample at 150 Torr with the unfiltered radiation (○, under illumination; ● in the dark).

assumption which led to the first tentative correlation between photoconductivity and photodesorption at room temperature (*3*, *4*, *5*). This assumption has, however, been questioned on the basis of successive irradiation experiments under different oxygen pressures (*13*). The conclusion of this paper was that oxygen desorbed in comparatively large amounts under illumination can not be responsible for the observed conductivity changes at room temperature. This observation and the fact that the photoconductivity does in any case depend on the ambient pressure point to the existence of at least two different types of chemisorption.

The existence of a weak type of chemisorption below about 200° was postulated by different authors and has more recently been directly identified by adsorption measurements (*7*). At temperatures below 200° the experimental evidence points to the existence of both a weak and essentially reversible type of oxygen chemisorption, and of a stronger type, essentially irreversible in the dark. Above about 300°C, on the contrary, only the strong type of chemisorption seems to be present.

The weak chemisorption has been tentatively associated with the presence of O_2^- or O^- adsorbed ions and the strong chemisorption with O^{2-} ions. Recent results (*16*) seem to indicate that the strong chemisorption is to be associated with excess zinc present on the surface. In order to interpret the results at room temperature one should therefore assume that weak chemisorption, which is largely effected by illumination, has only a very small effect on the conductivity, while strong chemisorption should cause large variation of the conductivity even with comparatively small variations of surface coverage.

This conclusion was also drawn by Barry and Klier (*10*). The possibility that small

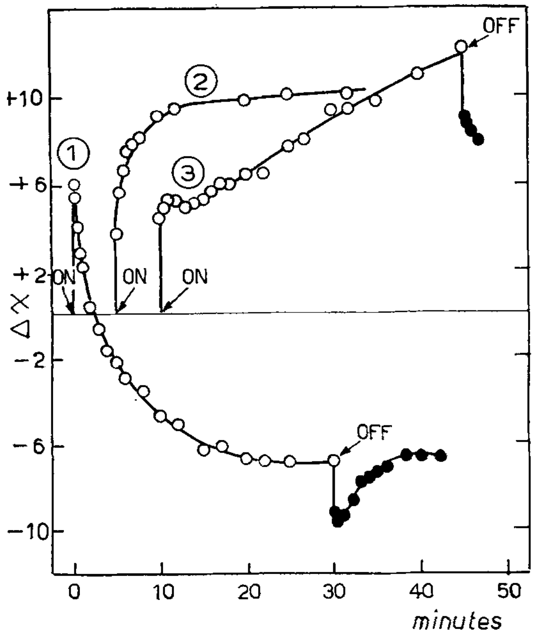

FIG. 11. Conductivity changes as a function of time under irradiation with the unfiltered radiation for different samples at 200°C and 150° Torr. Curve 1, Sample No. 5, fresh sample ($\Delta x \times 10^6$); Curve 2, Sample No. 4, pretreated in O_2 at 500°C ($\Delta x \times 5 \times 10^4$); Curve 3, Sample No. 6, pretreated in O_2 at 400°C ($\Delta x \times 10^7$).

variations of surface coverage entrain large variations of the conductivity has been pointed out by Mollwo, Stöckmann, and Heiland (*1*).

It therefore appears that the present results should be interpreted on the basis of a mechanism of adsorption and desorption of the strongly bound oxygen.

The Volkenstein Mechanism and the Dependence of the Kinetic Parameters on Experimental Conditions

In the mechanism of photoadsorption and photodesorption discussed by Volkenstein (*12*) it is assumed that upon irradiation a new electronic equilibrium is established almost instantaneously and that the system will adjust itself to the new equilibrium by adsorbing or desorbing oxygen, according to the sign of φ (see First part of the Discussion). At any instant the observed rate of adsorption (or desorption) will be given by the total rate of adsorption minus the total rate of desorption, until the two velocities become equal and a new adsorption equilibrium is reached. When irradiation is discontinued the system will again readjust to the initial electronic conditions by desorbing (or adsorbing) oxygen. This process is schematically illustrated by Fig. 14.

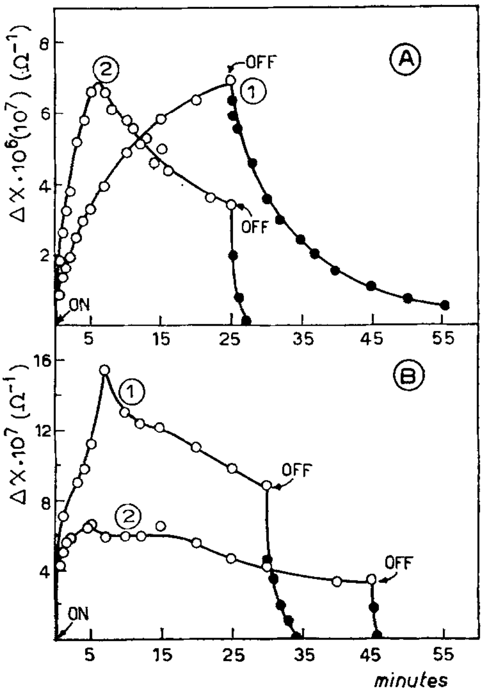

FIG. 12. Conductivity change as a function of time for Sample No. 6 (A) Sample pretreated in 230 Torr of O_2 at 400° for 145 min. Curve 1, unfiltered radiation ($\Delta x \times 10^6$); Curve 2, Filter 368 ($\Delta x \times 10^7$). (B) Sample pretreated in 60 Torr of O_2 at 400°C for 10 min. Curve 1, unfiltered radiation; Curve 2, Filter 2B.

If one assumes that for small variations of surface coverage, such as those presently involved, the conductivity depends linearly on the coverage [see ref. (*10*)], then the kinetics of the photoconductivity process will be similar to the kinetics of the chemisorption process.

The experimental results of Barry and Stone (*7*) show that the kinetics of both the adsorption and the desorption of oxygen in the dark can be approximated by Eq. (1)

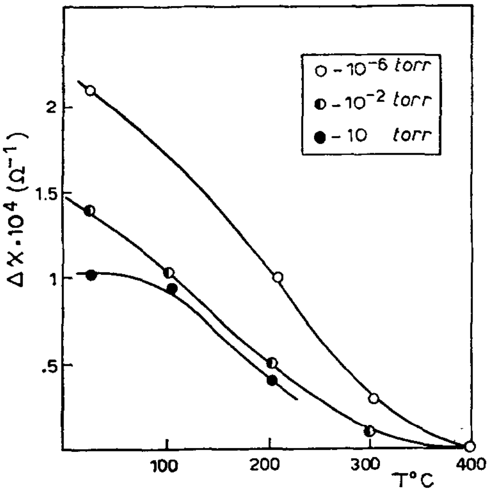

FIG. 13. A plot of the conductivity increase observed after 60 min of irradiation with the unfiltered radiation as a function of temperature, at different pressures. Sample No. 4 pretreated in high vacuum at 450°C.

at temperatures between 25° and 400°C. Equation (1) is therefore apt to describe the kinetics of both the weak and the strong type of chemisorption. It is also well known that Eq. (1) is of a rather general validity in chemisorption processes.

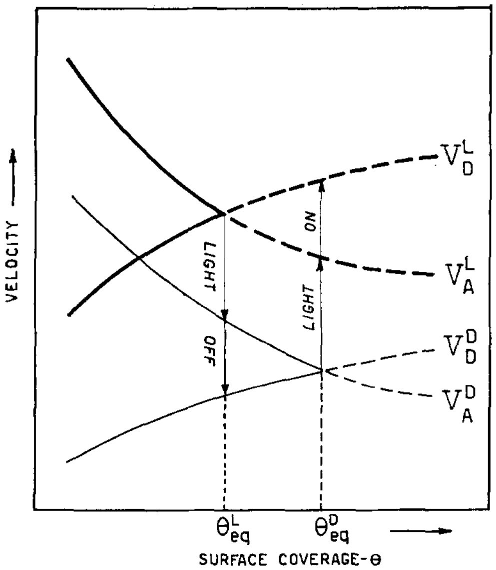

FIG. 14. Hypothetical plots of the velocity of adsorption and desorption in the dark (V_A^D, V_D^D) *and under illumination* (V_A^L, V_D^L) as a function of surface coverage.

The validity of this equation for both the conductivity rise and decay is therefore understandable. In fact the process of adjustment of the system to the modified electronic equilibrium, under or after illumination, is not essentially different from the adsorption or the desorption process in the dark (Fig. 14). However, the fact that at 25°C illumination always entrains a conductivity *increase* deserves comment. One should in fact be able to account for the observation that while both positive and negative photoeffects have been observed for the weak type of chemisorption only photodesorption occurs in the case of the strongly bound oxygen. According to Volkenstein (*12c*) the sign of the photoeffect is determined *inter alia* by the value of v (see beginning of the Discussion). This value will be different for the different forms of chemisorption, and should be smaller for the strong form. According to the treatment given in ref. (*12c*) only negative photoeffects might be expected for sufficiently small v values.

The dependence of the kinetic parameters of Eq. (1) on experimental conditions can now be examined.

The observed dependence of Δx_{60} on pressure (Fig. 4) is rather small in the pressure range 10^{-6}–10^{-2} Torr (of the order of $p^{-0.15} - p^{-0.06}$) and is practically zero above about 10^{-1} Torr. The observed dependence is difficult to account for quantitatively in that a number of factors have to be considered.

1. The "efficiency" of a *given decrease* of the surface coverage with oxygen in causing an *increase* of the surface conductivity should be lower the lower the initial conductivity in the dark, i.e. the higher the oxygen pressure. This point has been discussed by Heiland (*1*, *17*) and by Cimino *et al.* (*18*).
2. The *actual decrease* of surface coverage under illumination is determined by the shape and the relative positions of the curves of Fig. 14 and these are functions of the oxygen pressure.
3. At the higher pressures an additional mechanism of photodesorption, discussed in

the following, might contribute to the observed Δx_{60}, thereby decreasing the pressure dependence.

Similar arguments apply to the pressure dependence of the initial velocities a (or a^*) (Fig. 8).

One appreciates from Fig. 7 that α increases with increasing pressure and with decreasing light intensity. These results indicate that the deceleration of the process is higher the closer the equilibrium values of the conductivity are to the initial values in the dark.

The data of Tables 1 and 2 show that the values of $\Delta x_0^R/\Delta x_{60}$ and $\Delta x_0^D/\Delta x_{60}$ are both high on oxidized samples (up to 42%) and increase with increasing pressure. On reduced samples on the contrary the Δx_0 values for both the rise and the decay are either zero or small.

This observation implies, as discussed in a previous paper (*15*), that in cases where the Δx_0's are greater than 0, the process described by Eq. (1) is preceded by a different and faster process which follows a different kinetics. When $\Delta x_0 \cong 0$ one can assume that Eq. (1) is obeyed practically from the beginning of the process.

From the above considerations one might therefore conclude that the experimental results on reduced samples can be qualitatively understood in the light of Volkenstein's theory and of previous results. For oxidized samples, particularly at high pressures, the situation is more complex.

The Behavior of Oxidized Samples

In the case of oxidized samples one should be able to interpret the following observations:

(1) the presence of comparatively large $\Delta x_0/\Delta x_{60}$ values for *both* the rise and the decay, which increase with pressure (Tables 1, 2);

(2) the different behavior of oxidized and reduced samples in the experiments illustrated by Fig. 9;

(3) the dependence of the spectral sensitivity on the pressure which is observed on oxidized samples but not on reduced samples (Figs. 5 and 6);

(4) the complex behavior of the oxidized samples in the temperature interval between 100° and 300°C. (Figs. 10–12).

Previous results on fresh samples at room temperature should also be examined in connection with the present observations.

(1) According to results by Medved (*5*b) the saturation conductivity under illumination decreases with increasing wavelength at wavelengths longer than 400 mμ. Practically no photoconductivity was observed above about 600 mμ. Above about 430 mμ the author observes that the saturation photoconductivity in high vacuum is *smaller* than at 760 Torr.

(2) According to data by Mollwo and Stöckmann (*19*) for sintered fresh samples in air, plots of the initial rate of the conductivity increase as a function of wavelength shows a well-defined maximum at about 390 mμ or 410 mμ according to the type of sample. The rate falls to zero at about 600 mμ.

(3) In contrast to these results, the spectral dependence of the initial rates for thin ZnO films in high vacuum, as measured by Weiss (*20*), shows that the initial velocity is practically zero above about 390 mμ and increases at shorter wavelengths.

To interpret these results it will be assumed that on oxidized samples a second mechanism, always leading to photodesorption, is effective beside the Volkenstein mechanism.

The Mechanism of Photodesorption on Oxidized Samples

It is known that nearly stoichiometric ZnO shows a sharp optical absorption edge at about 385 mμ at room temperature, closely corresponding to the width of the forbidden gap. The presence of excess zinc in the crystal does, however, shift the absorption edge into the visible, this shift being larger the higher the concentration of excess zinc. Light absorption of nonstoichiometric ZnO has been observed up to about 600 mμ (*1*).

The perturbation introduced into the crystal by the stoichiometric excess therefore gives rise to centers which can absorb light at wavelengths up to about 600 mμ.

It will now be assumed that the energy absorbed by these centers during irradiation with light of appropriate wavelength can be transferred to chemisorbed oxygen atoms by a direct transfer mechanism, thereby favoring their desorption. It will also be assumed that energy can be transferred from these centers to surface oxygen only if the adsorbed atoms are located within a critical distance from the centers. The intensity of the energy transfer from the light absorbing centers to the adsorbed atoms will therefore depend on the following factors:

(1) the concentration of light absorbing centers, and their absorption coefficient at the wavelength of irradiation;
(2) the number of adsorbed atoms present within the critical distance, proportional to surface coverage;
(3) light intensity.

The detailed mechanism of energy transfer can not be specified at present. It might, however, be similar to one of the mechanisms which have been postulated for the transfer of energy from sensitizer to activator in luminescent materials (*21*). The concept of critical distance for energy transfer has also been derived from the theory of energy transfer in luminescent material.

As clearly shown by previous measurements (*22*) the amount of oxygen that can be adsorbed at room temperature on reduced samples is definitely smaller than the amount of oxygen present on the surface of oxidized samples. The mechanism of direct energy transfer should therefore prevail on oxidized samples. Upon irradiation chemisorbed atoms located within the critical distance will be easily desorbed, in that a fraction of the energy necessary for desorption will be provided by the transfer mechanism. A Volkenstein mechanism will, however, prevail beyond the critical distance, leading to adsorption or desorption of oxygen according to conditions. As a consequence, there will be patches on the surface which will be depleted of adsorbed oxygen much more than others. The rate of desorption corresponding to direct energy transfer will decrease with time as the critical areas are progressively depleted of adsorbed oxygen. After a certain time the rate of this process might become comparable to or even slower than the rate of desorption corresponding to a Volkenstein mechanism. When irradiation is discontinued the adsorption process will be very fast on the critical areas where surface coverage has become particularly low. One shall therefore expect to observe Δx_0 values for the decay process which will be larger the larger the Δx_0 values observed for the rise process, i.e. the larger the oxygen pressure and the higher the intensity of illumination.

(A) The behavior at 25°C. On the basis of the proposed mechanism one is therefore able to interpret:

(1) the dependence of the $\Delta x_0/\Delta x_{60}$ ratio on surface coverage;
(2) the correlation between the values of Δx_0 for the rise and the decay process;
(3) the results of Fig. 9.

Under conditions where the mechanism of direct transfer prevails the spectral dependence of the photoconductivity should closely be related to the spectral dependence of the optical absorption coefficients of the light absorbing centers. This observation allows one to interpret the spectral dependence of the initial rates observed by Mollwo and Stöckmann (*19*) and by Weiss (*20*), the spectral dependence of the saturation photoconductivity observed by Medved (*5*b), and the results of Figs. 5 and 6.

On oxidized samples at high pressure, the mechanism of direct energy transfer prevails and the largest contribution to the photoconductivity will therefore come from the centers which are responsible for the long wavelength tail of the optical absorption spectrum of ZnO. On reduced samples or on oxidized samples at low pressure these centers still contribute to the photoconductivity (Fig. 5, lower curve) but probably through a Volkenstein mechanism. The pressure dependence of the saturation photoconductivity above about 430 mμ reported by

Medved (*5*b) can also be understood along these lines.

(B) The behavior in the temperature interval 100°-300°C. The behavior of oxidized samples in this temperature interval can be understood on the assumption that both a Volkenstein and a direct transfer mechanism operate simultaneously.

As previously discussed, Volkenstein's theory predicts that at high oxygen pressures one should observe a change from photodesorption to photoadsorption as the temperature is increased. On the other end desorption by direct energy transfer will become less important as the temperature is increased. The results of Fig. 10, can therefore be understood in that desorption by direct energy transfer prevails within the critical areas while photoadsorption will become increasingly important outside these areas. The results of Fig. 11 illustrate the changes in the relative contribution of the two mechanisms brought about by different concentrations of adsorbed oxygen.

The observations of Fig. 11 are confirmed by curves 1 of Fig. 12A and B, while curves 2 confirm the view that the Volkenstein mechanism is more sensitive to wavelengths shorter than 385 mμ and the direct energy transfer mechanism to wavelengths longer than 400 mμ.

It should also be pointed out that the assumption of the simultaneous presence of the two mechanisms easily explains the observed minima in the kinetics in the dark and the rapid fall in the dark of the conductivity below the initial values (Fig. 10). In fact a rapid readsorption is expected in the dark within the critical areas together with a slower, temperature dependent desorption from the regions where adsorption has taken place during illumination.

ACKNOWLEDGMENTS

We wish to thank Profs. A. Cimino and F. S. Stone for stimulating discussion and Dr. G. Ghersini for his help in performing some of the experiments. Partial support of this work by the National Research Council of Italy is gratefully acknowledged.

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