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Heterogeneous Photocatalysis I. The Influence of Oxidizing and Reducing Gases on the Electrical Conductivity of Dark and Illuminated Zinc Oxide Surfaces

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Since the photoconductivity of zinc oxide increases with time in a carbon monoxide atmosphere and also during the subsequent evacuation under light, it must be concluded that the uptake of CO by an illuminated zinc oxide surface is understandable only if neutral CO molecules react with chemisorbed oxygen to form CO_2^-(ads). The decreased photoconductivity of zinc oxide due to introduction of carbon monoxide in oxygen confirms this mechanism and leads to the further assumption that a considerable portion of the chemisorbed oxygen must be present as O_2^-(ads). This assumption also explains why the half-life period $t_{1/2}$ of the dark decay in pure oxygen is proportional to $1/p_{O_2}$.

The generation of charge carriers during the illumination is strongly influenced by doping zinc oxide with Li_2O and Ga_2O_3. Possible mechanisms are discussed. Since an addition of Li_2O to zinc oxide changes neither the position nor the intensity of the green luminescence band, it remains uncertain whether the donors, reacting with the electronic species, are responsible for the green luminescence light.

INTRODUCTION

Previous investigations have shown that conductivity of semiconductors, e.g., Cu_2O, NiO, ZnO, CdS, and PbS, is significantly influenced by gases not only at high temperatures but also at low temperatures. This change in conductivity is caused by a chemisorption or by a reaction of the appropriate gas with the semiconductor and is connected with an electron transfer process. Since many catalytic reactions at surfaces of solids are initiated by a chemisorption of one or several reactants, this phenomenon is not only of interest in semiconductor investigations but also is of importance in understanding heterogeneous catalysis. Hence, such problems are being studied by chemists and physicists interested in the behavior of semiconductors and in the catalytic properties of solids. At present, the dominant problem is the dependence of the gas uptake of a semiconductor on its lattice defect structure. An obvious approach is to change the concentration of holes, free electrons, or lattice defects by a definite amount in a *p*-type and an *n*-type semiconductor by appropriate gas treatment or by doping with foreign ions of different valence (e.g., Ga^{3+} or Li^+ in zinc oxide) and to study the influence of this doping on the course of heterogeneous catalytic reactions with the semiconductor. This technique offers only one type of charge carrier (holes or free electrons) to the reacting gas, but photoconducting solids offer both electrons and holes by illumination. Therefore, we have studied the influence of oxygen and carbon monoxide, both alone and together, on the dark- and photoconductivity of pure and doped zinc oxide, a well-investigated photoconductor (*1*).

Zinc oxide, an *n*-type semiconductor, can be described by a metal excess represented either by zinc ions in interstitial lattice positions, $Zn^{\cdot}$ or $Zn^{\cdot\cdot}$, or by oxygen-ion vacancies,

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$|0|^{\cdot}$ or $|0|^{\cdot\cdot}$ with an equivalent number of free electrons e'.* At sufficiently high temperatures (800° and 1000°C) the equilibrium is established between the gas atmosphere and the lattice defects (2):

$$1/2O_2\ (\text{gas}) + Zn^{\cdot\cdot} + 2e' \rightleftarrows ZnO \tag{1}$$

and/or

$$1/2O_2\ (\text{gas}) + |0|^{\cdot\cdot} + 2e' \rightleftarrows \text{Nil} \tag{2}$$

According to extensive investigations it must be assumed that at lower temperatures the electronic exchange equilibria

$$Zn^{\cdot\cdot} + e' \rightleftarrows Zn^{\cdot} \tag{3}$$

or

$$|0|^{\cdot\cdot} + e' \rightleftarrows |0|^{\cdot} \tag{4}$$

are shifted far to the right. Therefore, in the temperature region covered in this work, (25–250°C) practically only $Zn^{\cdot}$ or $|0|^{\cdot}$ lattice defects are present. Furthermore, due to the different mobilities of the lattice defects and the free electrons the reaction of the gas with the electrons only—the so-called chemisorption—is faster by several orders of magnitude than the subsequent reaction of chemisorbed oxygen with lattice defects. Under our experimental conditions, especially at short reaction times, we have to consider predominant chemisorption of oxygen with a positive space-charge layer near the ZnO surface.

$$O_2\ (\text{gas}) \rightleftarrows O_2^{x}\ (\text{ads})\ \text{Physisorption} \tag{5}$$

$$O_2^{x}\ (\text{ads}) + e'(R) \rightleftarrows O_2^{-}\ (\text{ads})\ \text{Chemisorption} \tag{6}$$

The ^{x} denotes the electrically neutral state and R the space-charge layer. The process is characterized by a negative surface charge represented by the chemisorbed O_2^- ions, and by a positive space charge represented by an excess of zinc ions in interstitial lattice positions due to the exhaustion of free electrons (*3*). On the basis of our experiments it can be assumed that a considerable amount of chemisorbed oxygen exists as negatively charged molecules. Experimental techniques to determine the amount of O^- particles on the surface are not yet available.

From the results of studies of the low-temperature oxidation of zinc metal, it appears that part of the chemisorbed oxygen must react with the zinc ions in interstitial lattice positions—the so-called donors—in the space-charge layer (*4*):

$$O_2^-\ (\text{ads}) + Zn^{\cdot}\ (R) + e'(R) \rightarrow ZnO + O^-\ (\text{ads}) \tag{7}$$

$$O^-\ (\text{ads}) + Zn^{\cdot}\ (R) \rightarrow ZnO \tag{8}$$

With increasing temperatures the extent of the last two reactions can become larger than the chemisorption, as has been shown for the reaction of carbon monoxide with nickel oxide (*5*). To obtain further information about the mechanism of gas reactions on solid surfaces we have investigated the effect of oxygen and carbon monoxide on the conductivity of dark and illuminated zinc oxide. In a subsequent paper, an investigation of the oxidation of carbon monoxide on zinc oxide is presented (*6*).

The Uptake of Oxygen and Carbon Monoxide on Illuminated Zinc Oxide Surfaces

During the illumination of zinc oxide with light of 380 mμ (i.e., in the region of optical self-absorption of zinc oxide) electron–hole pairs, $e' \sim |e|^{\cdot}$, are produced in the surface region of the crystal to a depth of 10^{-5} cm:

$$h\nu\ (380\ m\mu) \rightarrow e' \sim |e|^{\cdot} \tag{9}$$

The wavy line between e' and $|e|^{\cdot}$ denotes the exciton character of the electron–hole pairs which, in this coupled state, do not contribute to the electrical conductivity. Only if one of the two species of the electron–hole pairs, especially the hole, can react with trapping centers within the crystal or at the surface, the remaining free electrons act as charge carriers. It is remarkable that with trapping centers the holes react more readily than the free electrons. Obviously, in the *n*-type ZnO the holes generated by the illumination seem to be "foreign species" and will disappear preferentially. This fact

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* We use the symbols of W. Schottky, *in* "Halbleiterprobleme," Vol. 4, p. 235. Vieweg-Verlag, Braunchweig, 1959. Here $Zn^{\cdot}$ or $Zn^{\cdot\cdot}$ denote ions in interstitial lattice position and $|0|^{\cdot}$ or $|0|^{\cdot\cdot}$ denote ion vacancies. The dots indicate the number of positive charges. Furthermore, e' is a free electron with a prime to indicate negative charge and $|e|^{\cdot}$ is a hole with a dot to indicate positive charge. Nil denotes that no disorder is present.

is important in the reaction mechanisms of chemisorption and desorption of gases.

Experimental Apparatus and Procedure

All measurements were carried out with polycrystalline, compressed zinc oxide samples which were finally sintered at high temperatures in atmospheres of various oxygen pressures. In order to avoid barrier-layer effects (deviations from Ohm's law) the following electrode system was employed:

Ag|graphite|ZnO|graphite|Ag

The dimensions of the samples prepared from spectroscopically pure zinc oxide were 20 × 20 × 4 mm and the illuminated geometric surface was 4 cm². The electrical field strength, generally, amounted to approximately 15 to 20 volt/cm and the wavelength of the illuminated light was 365 mμ. The light source was a high-pressure mercury vapor lamp HBO 500 (Osram). With a quartz lens (100-mm focal distance) an approximately homogeneous distribution of the incident light was obtained. The most effective mercury light of 365 mμ was isolated by a combination of two colored glass filters: UG 11 and BG 38 (Schott & Gen.). In addition, an iris diaphragm and a shutter were inserted into the light beam.

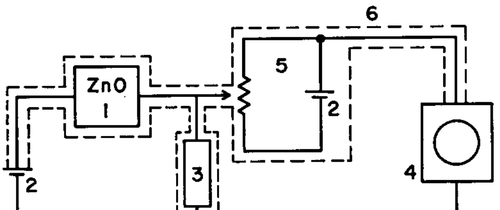

FIG. 1. Block diagram for conductivity measurements. 1, Zinc oxide sample; 2, anode battery; 3, resistance of 10^3 to 10^5 ohms; 4, oscilloscope (Tektronix type 535A); 5, compensation bridge for adjusting the position of the electron beam; and 6, grounded shielding.

As shown in the block diagram in Fig. 1, the sample of zinc oxide was connected in series with a working resistance which transformed the change of the photocurrent with time due to the illumination into a corresponding voltage change. This change of voltage was measured by means of an oscilloscope (Tektronix Model 535A) with a voltage amplifier in a compensation bridge. The oscilloscope traces were photographed and evaluated. The dark-conductivity as a function of temperature and gas pressure was measured by the same method. In the case of ZnO samples with resistances greater than 10^6 ohms the input resistance of the oscilloscope was in series with the zinc oxide sample. In order to obtain undisturbed measurements with the oscilloscope at electrical field strengths as low as 10 mv/cm, the anode battery, the resistance bridge, and the measuring chamber (except the window for the illumination) were shielded and grounded.

Figure 2 represents the measuring chamber with the preheating vessel for the entering gas. The rectangular sample was fixed to a glass support, h, through which a thermostatted fluid was circulated. By this arrangement the temperature could be maintained constant at any desired value between −100 and +100°C. For measurements at higher temperatures (up to +200°C) the measuring chamber was wound with a heating tape. The temperature was controlled by a regulator to about ±2°C. The temperatures in chambers A and B were recorded separately. Both chambers were evacuated and after attainment of temperature equilibrium could be connected by the stopcock k. The gases were purified by standard methods.

All zinc oxide samples, pure and doped with Li_2O or Ga_2O_3, were annealed at 850°C for 5 hr either in oxygen at 1 atm or in vacuum at 10^{-4} Torr. In order to prevent a reaction of zinc oxide with the material of the furnace during the annealing process all samples in the furnace were placed on other ZnO samples which were not used for measurements (*7*). After putting contacts on both ends of the annealed samples they were placed between two platinum electrodes b and d. Satisfactory electrical contact was secured by applying a slight pressure with the help of steel springs.

Reaction of Oxygen with Charge Carriers at the Surface of Zinc Oxide

As reported in the literature, the extent of photoconductivity and its decay are de-

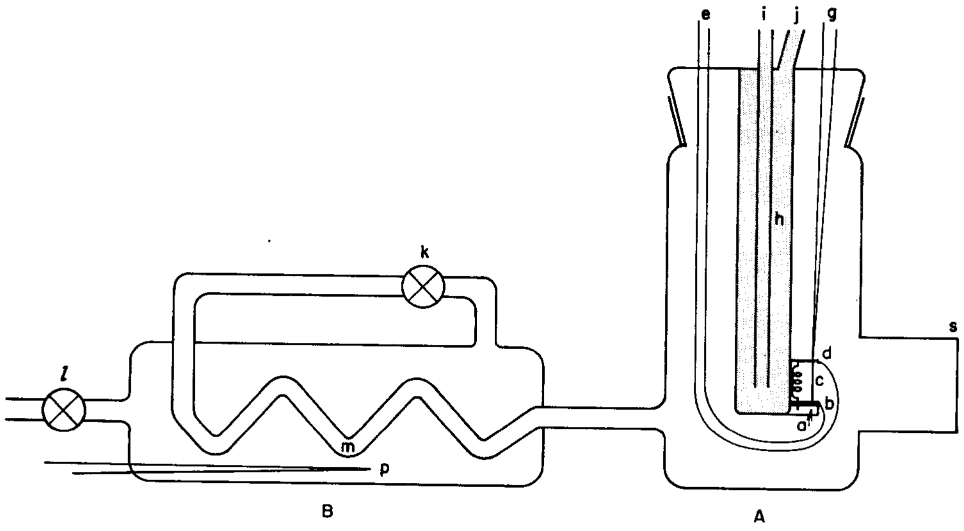

FIG. 2. Measuring chamber and preheating vessel containing glass support with the zinc oxide sample. A, Measuring chamber; B, preheating vessel; l and k, stopcocks for the entrance of the gas mixture; m, preheating coil; h, glass support with sample holder, a, and the platinum electrodes b and d (between them the ZnO sample c); e and g, ground stoppers for the current supply and the thermocouple; i and j, tubes for connection with a circulation thermostat; s, window for illumination; p, thermocouple.

pendent on the oxygen pressure. In the presence of oxygen, and also after later addition of oxygen, the decay is strongly increased compared to that observed in high vacuum. The curves of Fig. 3 were obtained at 160°C. It can be concluded from these measurements that the steady state of the photoconductivity is determined only by the oxygen pressure, independently of whether the oxygen is already present at the beginning of the illumination or is later added during the illumination. This conclusion is confirmed by the results shown by the curves 2 and 7 of Fig. 3 in the one case and curves 3

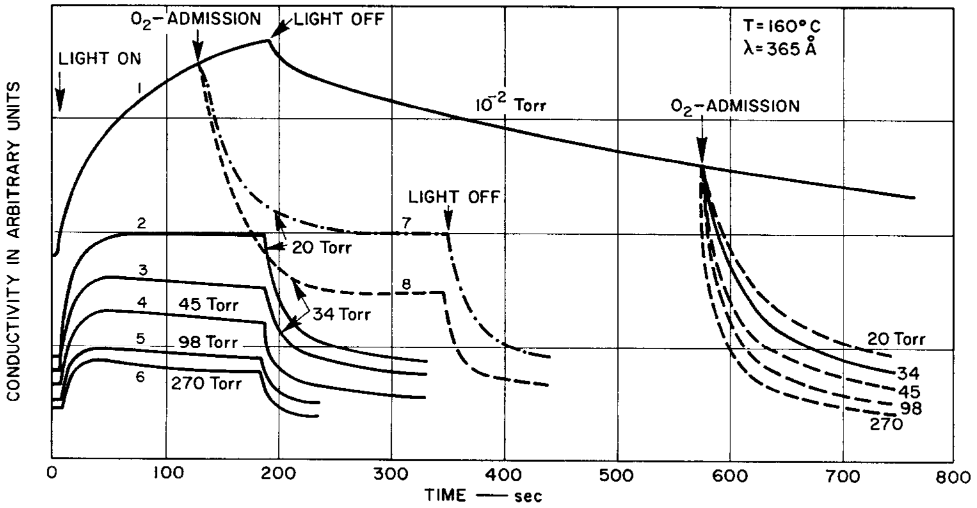

FIG. 3. Variation with time of the dark- and photoconductivity of zinc oxide at 160°C and various oxygen pressures. (O_2 admission during illumination and during the dark-decay is indicated by arrows on curves 7 and 8.)

and 8 in the other case. Without doubt the oxygen pressure is of great influence on the extent of the generation of charge carriers. While in the experiments represented by curves 2 and 3 oxygen will be desorbed, curves 7 and 8 indicate an adsorption of oxygen during illumination.

These experimental results are in agreement with those of other authors. For instance, Medved (*8*) could demonstrate the desorption of oxygen by simultaneous measurements of the electrical conductivity and of the gas pressure. The inverse step of an oxygen uptake at illuminated zinc oxide surfaces was first studied by Mjasnikov (*9*) and extended by Barry and Stone (*10*) by means of conductivity and pressure measurements.

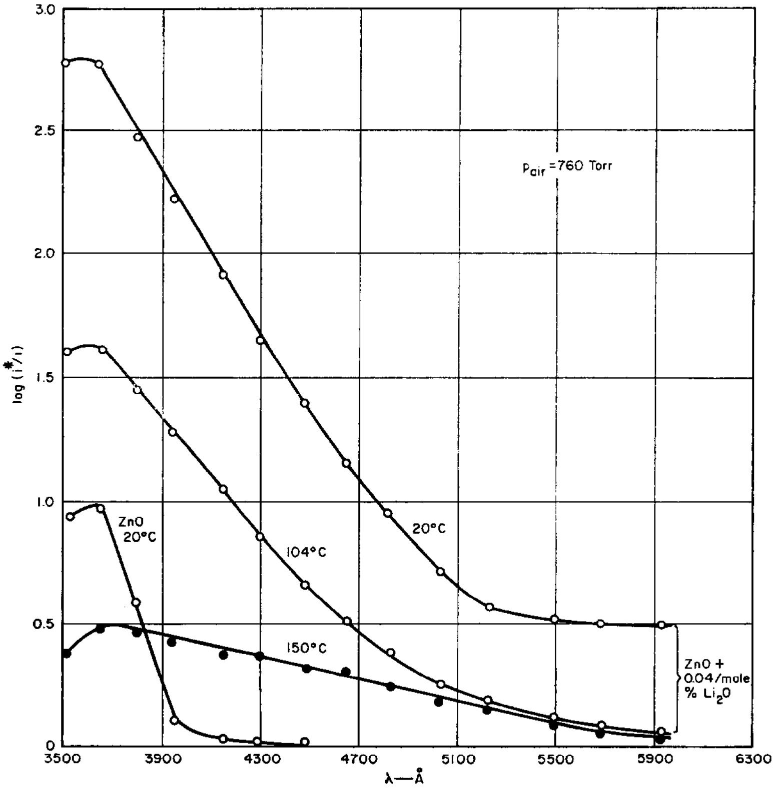

FIG. 4. Ratio of the photocurrent i^*, and dark current, i, at various temperatures as function of wavelength for pure zinc oxide and for zinc oxide doped with 0.04 mole % Li_2O in air at 1 atm.

In the case of Li_2O doping, even an addition of a small amount of Li_2O (~0.04 mole %) has a remarkable influence on the photoconductivity. As shown in Fig. 4, the ratio of the photo- and dark-current $i_{light}/i_{dark} \equiv i^*/i$ is increased by approximately 2 orders of magnitude of 20°C. The optical absorption and the photoconductivity of pure zinc oxide commence sharply at $\lambda = 400$ mμ with a steep increase and reach their maximum value at 370 mμ, but the photoconductivity and the optical absorption (Fig. 5 represents the optical reflection which is equivalent to the optical absorption) of zinc oxide doped with lithium oxide are already observable at longer wavelengths. Furthermore, Fig. 4 shows that the ratio i^*/i is decreasing with increasing temperature and attains only one-half power of ten at 150°C. In contrast to the increase of the ratio of photo-to-dark conductivity of zinc oxide doped with Li_2O, the ratio of the conductivities of zinc oxide doped with Ga_2O_3 was only one-fifth of the ratio for pure zinc oxide.*

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* According to Hauffe (*11*) a milling process decreases the photoconductivity of pure and doped ZnO.

The dependence of dark- and photoconductivity on temperature and oxygen pressure. As reported in the literature (*12*) the conductivity of ZnO at low temperatures (e.g., 25°C) can be changed by several orders of magnitude by a pretreatment at a suitable temperature and gas atmosphere. This can be realized, for instance, by annealing zinc oxide in high vacuum at high temperatures and subsequently dropping to low temperatures (25°C) to measure the conductivity at 1 atm of oxygen between 25° and 250°C both in the dark and under illumination. Tischer (*13*) found a linear relationship between the dark- and photoconductivity. If the dark-conductivity of pure zinc oxide, however, is too large, the photoconductivity is practically no longer observable; obviously, the additional charge carriers generated by light represent only a relatively small addition to the large concentration already present in the dark. In contrast to this result, for zinc oxide doped with lithium oxide the increase of charge carriers by illumination has a great influence on the conductivity under all experimental conditions as long as the temperature is not too high. Figure 6 represents the dependence on the temperature of the dark- and photoconductivity of zinc oxide doped with 0.04 mole % Li_2O at 1 atm air. Here the ratio $\sigma_{light}/\sigma_{dark}$ attains the value of one at approximately 200°C because of the different slopes of the curves.

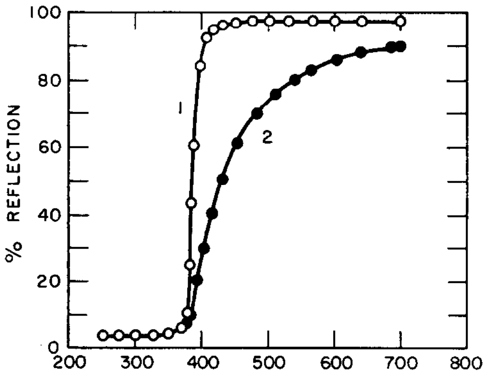

FIG. 5. Wavelength dependence of the reflection spectra of pure zinc oxide (curve 1) and zinc oxide doped with 0.05 mole % Li_2O (curve 2) versus $BaSO_4$ as reference substance at 20°C.

In further experiments the dependence of both the dark- and photoconductivity of zinc oxide on the oxygen pressure has been measured at 150°C and at decreasing and increasing oxygen pressure (Fig. 7). Deviations in the absolute values of the conductivity depend on whether the oxygen pressure increases or decreases. These deviations are not surprising at low-temperature measurements because especially in this temperature region the highly sensitive surface equilibria are determining the conductivity in the space-charge layers, while at high temperature the concentration of the charge carriers in the bulk, in equilibrium with oxygen, is responsible for the conductivity. The exponent of the oxygen-pressure dependence of the dark- and photoconductivity at 25°C is approximately the same. While the exponent of the oxygen-pressure dependence of the dark-conductivity with decreasing oxygen pressure ($\sigma \sim p_{O_2}^{-1/2}$) is in fair agreement with that quoted by Engell and Hauffe (*14*), the corresponding value obtained with increasing oxygen pressure is somewhat lower: $\sigma \sim p_{O_2}^{-1/2.7}$.

Luminescence Measurements with Pure and Doped Zinc Oxide

Nicoll (*15*) found that zinc oxide exhibits two luminescence bands during illumination with light of 365 mμ or during irradiation with electrons of a corresponding energy. One of the bands has its maximum at 25°C at $\lambda = 390$ mμ—this is very near the edge of the self-absorption band —and the other at $\lambda = 510$ mμ. Since the longer green wavelength band was expected to be caused by the recombination of free eletcrons with the double-charged donors $Zn^{\cdot\cdot}$ during the illumination:

$$Zn^{\cdot\cdot} + e' \rightarrow Zn^{\cdot} \quad (10)$$

it seemed desirable to measure the luminescence of zinc oxides subjected to different pretreatments and doping with Li_2O. The results of these measurements are presented in Fig. 8.

On the illuminated outer surface of the measuring cell in the fluorescence attachment of the spectrophotometer, a fast-drying colorless adhesive was supported and the grains of the milled zinc oxide pellets were

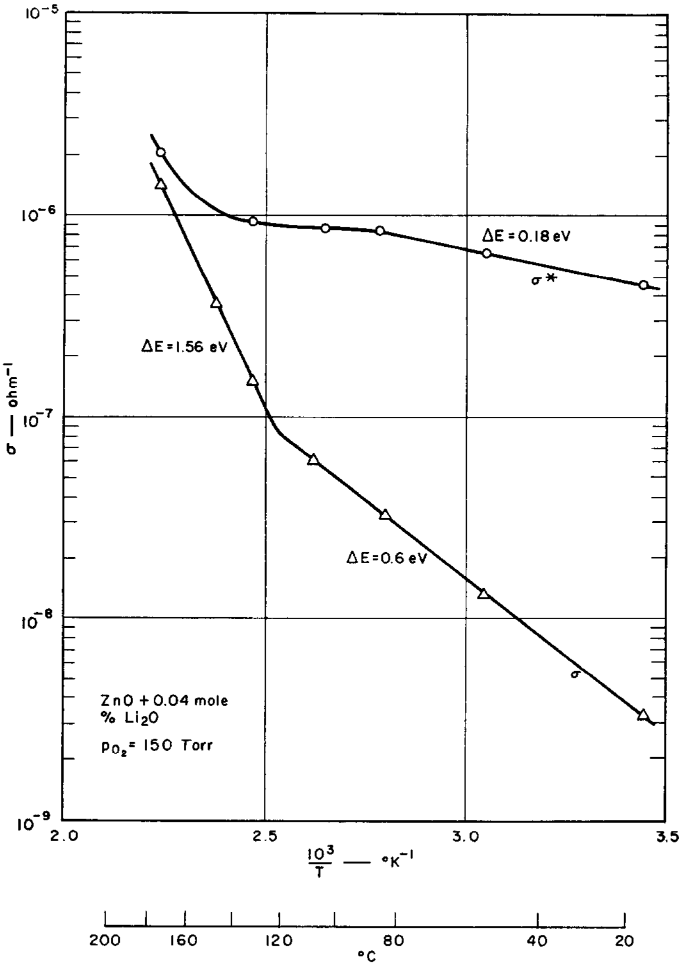

FIG. 6. Temperature dependence of the dark- and photoconductivity of zinc oxide doped with 0.04 mole % Li_2O at $P_O = 150$ Torr.

sprinkled on it. The fluorescence attachment was thermostatted at a definite and constant temperature between 25° and 80°C. Our experimental arrangement did not permit the determination of absolute values of the luminescence. After our experiments both the wavelength and the intensity of the green (λ = 510 mμ) luminescence band could not be noticeably changed, either by annealing or by doping of the zinc oxide sample. In spite of a large increase of the donor concentration in zinc oxide due to an addition of 0.2 mole % Li_2O, an increase of the intensity of the green luminescence band was not detectable. Therefore, it remains uncertain whether the electronic reaction *(10)* is responsible for the green luminescence light.

The Reaction of Carbon Monoxide with the Zinc Oxide Surface

Elucidating results have been obtained by the study of the influence of carbon monoxide on the dark- and photoconductivity of ZnO. According to gas-volumetric measurements at low pressures (10^{-2} Torr) by Terenin and Solonitzin *(16)* light of 365 mμ promotes the uptake of carbon monoxide on zinc oxide. This result at first suggests that the uptake of carbon monoxide can be explained by a mechanism similar to the oxygen chemisorption, i.e., either by a direct reaction with the emission of electrons in the dark or by recombination with the electron–hole pairs during illumination:

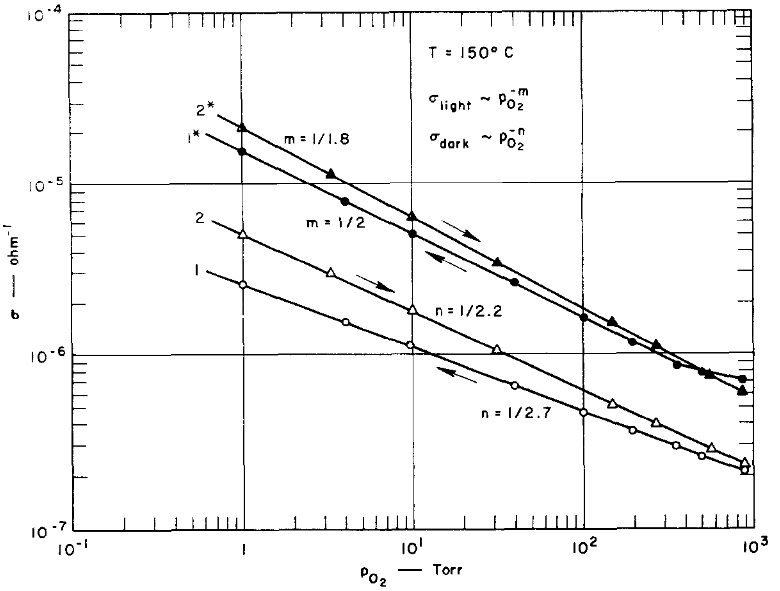

FIG. 7. Oxygen-pressure dependence of the dark- and photoconductivity of zinc oxide with oxygen pressure at 150°C. (Time between sets of measurements was 12 hr; photoconductivity measurements made after an illumination time of 10 min.)

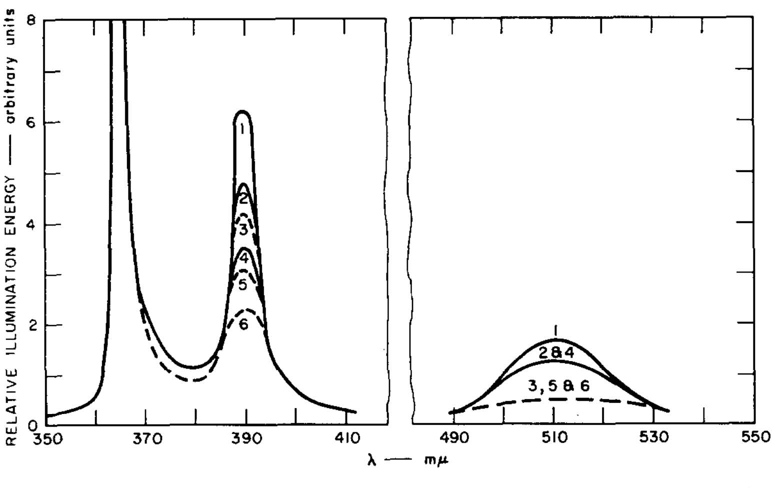

FIG. 8. Dependence of luminescence of zinc oxide on pretreatment and doping (excitation, 365 mμ). ZnO untreated: (1) at 25°C, (4) at 80°C. ZnO pretreated at 850°C in oxygen: (2) at 25°C, (5) at 80°C. ZnO doped with 0.2 mole % Li_2O: (3) at 25°C, (6) at 80°C.

$$\text{CO (gas)} \rightleftarrows \text{CO}^+ \text{ (ads)} + e' \text{ in the dark} \quad (11)$$

$$\text{CO (gas)} + |e|^{\cdot} \sim e' \rightarrow \text{CO}^+ \text{ (ads)} + e' \text{ under light} \quad (12)$$

whereby free electrons result which are preferentially available for the charge transport. This evident mechanism, however, cannot explain the following experimental results.

If a zinc oxide sample is illuminated at 160°C in a carbon monoxide atmosphere of 45 Torr, an increase of the conductivity is observed. The curve, represented in Fig. 9, has a slope similar to that of the photoconductivity in high vacuum. The absolute value of the photoconductivity in carbon monoxide, however, is somewhat smaller after a longer illumination period than that

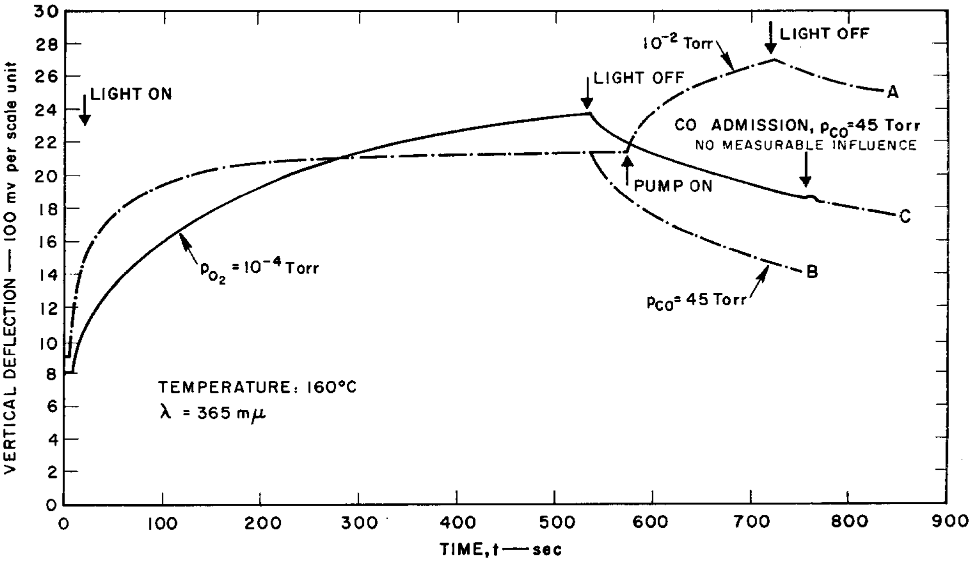

FIG. 9. Course of photoconductivity and of dark decay with time of zinc oxide in vacuum and in carbon monoxide at 160°C.

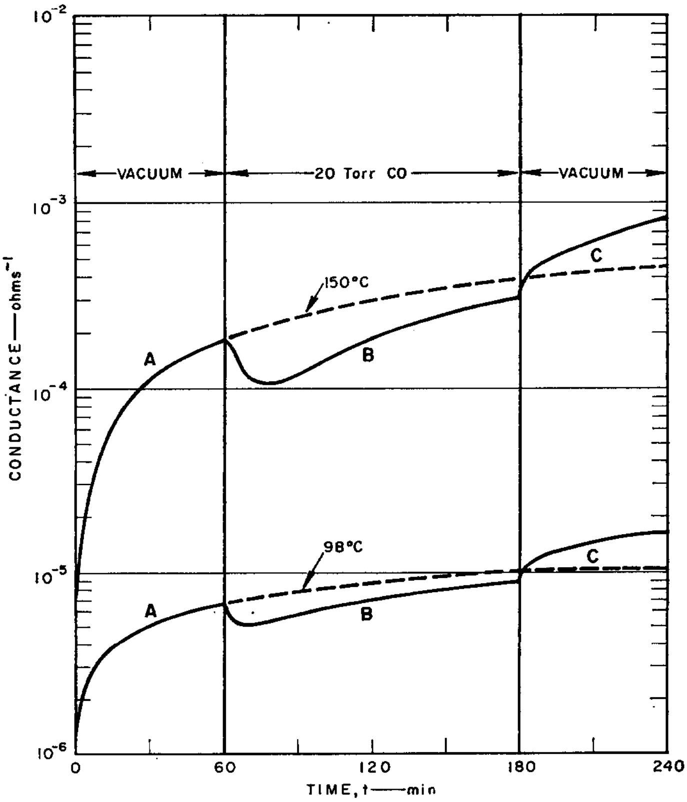

FIG. 10. Change of dark-conductivity of pure zinc oxide with time. Sequence of measurements: (A) under vacuum, (B) under CO of 20 Torr, and (C) under vacuum. ZnO was pretreated 5 hr in air at 1 atm and 850°C.

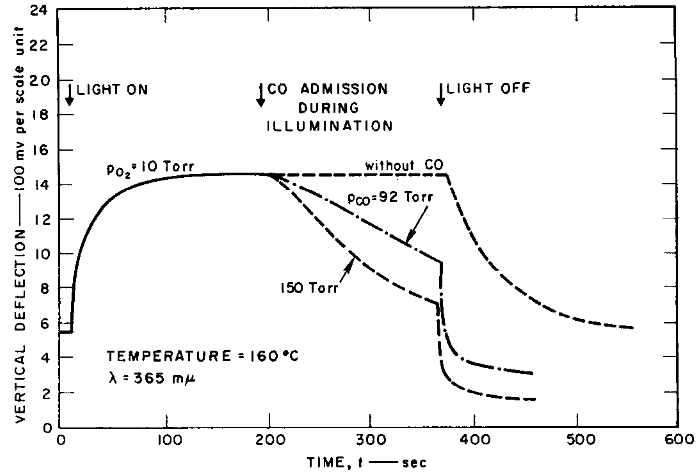

FIG. 11. Change of the photoconductivity with time of zinc oxide doped with 0.04 mole % Li_2O.

in high vacuum. The decay of the conductivity in the dark period also follows practically the same course as that in high vacuum (see curve B in Fig. 9). Noticeable is the fast appearance of the steady state of the photoconductivity of zinc oxide in carbon monoxide which remains constant at longer illumination periods. Furthermore, during continuous illumination in vacuum an additional increase of the photoconductivity is observed (see curve A in Fig. 9).

A similar influence of carbon monoxide on the dark-conductivity of zinc oxide was observed. As shown in Fig. 10, the desorption of oxygen detectable by the increase of the conductivity with time is stopped by introduction of CO. During the further action of carbon monoxide on zinc oxide, however, the conductivity increases slowly without reaching the dotted curve which would be obtained if the evacuation were not interrupted by a CO treatment. If, after a period of time, the vacuum is restored, a noticeable increase of conductivity occurs which is larger than that of the vacuum-treated zinc oxide. These phenomena seem to be based on the same mechanism as those observed under illumination.

In order to obtain information on the mechanism of the reaction of carbon monoxide with the chemisorbed oxygen at the zinc oxide surface, carbon monoxide was intro-

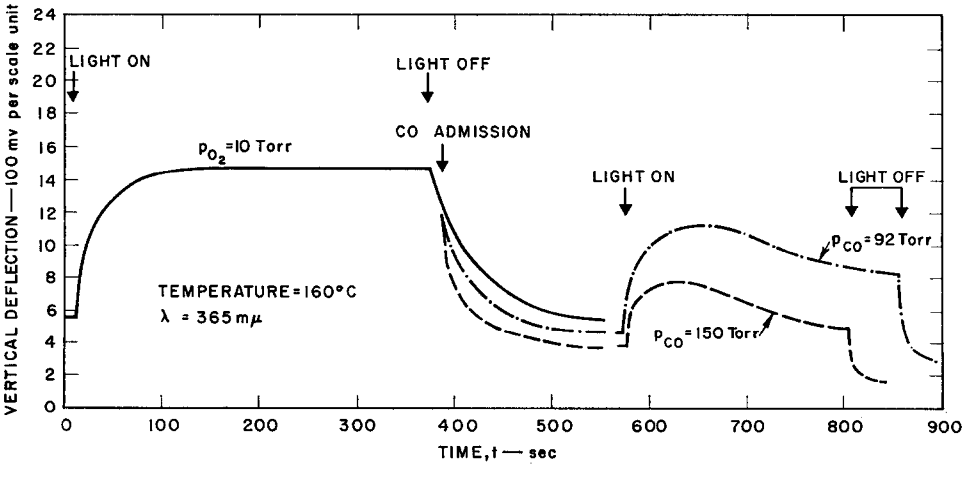

FIG. 12. Conductivity measurements with the same zinc oxide sample as in Fig. 11.

duced at 92 and 150 Torr into the reaction chamber which contained the zinc oxide sample doped with 0.04 mole % Li_2O under 10 Torr oxygen at 160°C. Figure 11 shows that by introduction of CO during the illumination, the photoconductivity is not only decreased but also the dark decay becomes considerably faster and attains values below the original value of the dark-conductivity before illumination. Finally, carbon monoxide was introduced in the chamber with the same zinc oxide sample under the same experimental conditions as above, but only during the dark period, whereupon the dark-decay rate increased (Fig. 12). On repetition of the illumination, now in the presence of a gas mixture of 10 Torr oxygen and 92 or 150 Torr carbon monoxide, is considerably below the value attained at 10 Torr oxygen only. Furthermore, the photoconductivity decreases continuously during the illumination. The value of the dark-conductivity resulting from the steep dark decay is still lower than that of the preceding experiment.

Discussion of the Experimental Results

From the experiments described in the preceding section we conclude that the generation and annihilation of charge carriers—free electrons in zinc oxide—are influenced by the presence of oxygen. The influence of carbon monoxide on these processes is more complicated because of a chemical reaction of carbon monoxide with the chemisorbed oxygen, along with participation of free electrons in the zinc oxide surface, which will be discussed below in more detail. Recently Kokes (*17*) reported two types of oxygen chemisorption measured by means of electron spin resonance; one appears at room temperature as O^- species and the other appears at 200°C (or above) as O^{2-} species. The latter is stabilized by migration of donors to the surface in the formation of ZnO as has been described above [see Eqs. (7) and (8)]. The method used by Kokes did not permit a distinction between O^- and O_2^- species.

From the dependence of the photoconductivity on the oxygen pressure, one may tentatively conclude that electron–hole pair formation cannot be directly responsible for the increase of the conductivity during illumination. A photochemical reaction must play a decisive role whereby the holes react with the chemisorbed oxygen species at the surface in order to uncouple the excitons $|e|^\bullet \sim e'$

$$\begin{aligned} O_2^- \text{ (ads)} + |e|^\bullet \sim e' &\rightarrow O_2^x \text{ (ads)} + e' \\ &\rightarrow O_2 \text{ (gas) desorption} \end{aligned} \tag{13a}$$

and

$$O^- \text{ (ads)} + |e|^\bullet \sim e' \rightarrow O^x \text{ (ads)} + e' \tag{13b}$$

$$O^x \text{ (ads)} + O^- \text{ (ads)} \rightarrow O_2^- \text{ (ads)} \tag{13c}$$

where reaction (13c) is followed by reaction (13a). Without doubt, such an uncoupling process requires still other reaction centers both at the surface and within the crystal to be taken into consideration. In addition to these desorption reactions, a chemisorption according to Eqs. (5) and (6) can take place (see Fig. 3). The extent of these reactions depends on the oxygen pressure. In any case a steady state is established; it is characterized by a definite concentration of free electrons responsible for the photoconductivity. The contribution of the holes to the conductivity should be negligible.

On the basis of this mechanism one may conclude that the Fermi potential in zinc oxide retains its definite thermodynamical meaning even in the illuminated state, since in any case only free electrons are charge carriers (the concentration of holes is too low due to their reaction with the chemisorbed oxygen). The value of the Fermi potential is independent of the concentration of the exciton-like electron–hole pairs. In this situation the concept, occasionally mentioned in the literature, that the Fermi potential of an illuminated crystal loses its meaning and is to be substituted by two independent chemical potentials μ_- and μ_+ cannot be maintained.

After switching off the light, the disturbed electronic equilibrium caused by the electrons produced in excess will diminish again to its thermodynamic equilibrium because of the reaction of the excess free electrons with electron-affinity centers, such as physisorbed oxygen, double-charged donors $Zn^{\bullet\bullet}$, or other lattice defects. Therefore in a crystal with small concentrations of lattice defects the rearrangement of the thermodynamic equilibrium can be preponderantly understood by the mechanism described above by Eqs. (5) through (8).

It may be concluded that a considerable portion of the chemisorbed oxygen must be present as O_2^-(ads) not only from the reaction of the chemisorbed oxygen with carbon monoxide, discussed later, but also by the evaluation of the half-life period $t_{1/2}$ of the dark decay as a function of the oxygen pressure. This is seen in Fig. 13 where $t_{1/2}$ plotted against $1/p_{O_2}$ yields a straight line, but only up to $t_{1/2} = 20$ sec. Above this value the deviations become larger and larger. This, however, is not surprising if one considers that the relation $t_{1/2} \sim 1/p_{O_2}$ is based on the assumption that as a rough approximation only the forward step of the chemisorption in Eq. (6) shall be rate-determining. Therefore, we obtain for the rate of decrease of the concentration of free electrons, $\dot{c}_- \equiv dc_-/dt$:

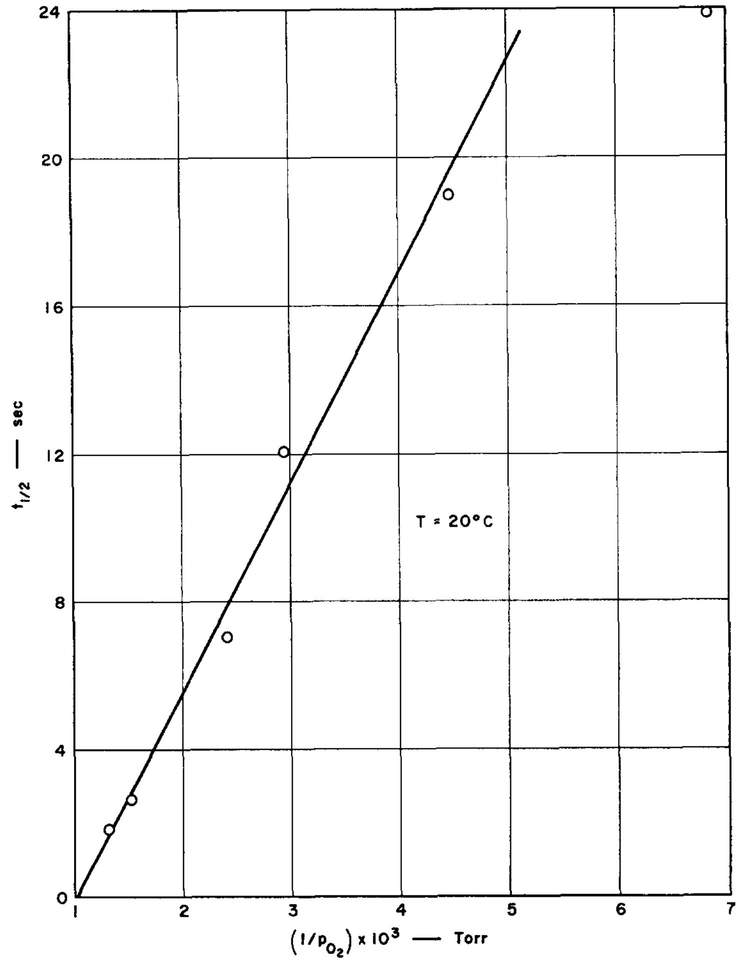

FIG. 13. Half-life versus the reciprocal oxygen pressure. Values obtained from measurements of the oxygen-pressure dependence of the dark decay at 20°C.

$$\dot{c}_- = k_2 K_1 c_- p_O. \tag{14}$$

where K_1 is the equilibrium constant of the law of mass action for the physisorption, Eq. (5), and k_2 the rate coefficient of the forward step of reaction, Eq. (6). Furthermore, if one considers that the conductivity σ is proportional to c_- and if Eq. (14) is integrated between the limits $t = 0$ and $t = t_{1/2}$

and $\sigma(\max)$ and $\sigma(\max)/2$, respectively, we obtain:

$$t_{1/2} = [\sigma(\max)/2k_2K_1](1/p_{O_2}) \qquad (15)$$

From the slope of the straight line in Fig. 13, the rate constant k_2 of the chemisorption can be determined if $\sigma(\max)$ and K_1 are known from other measurements.

As can be concluded from long-time illumination experiments in high vacuum at 150°C, not only chemisorbed oxygen desorbs according to Eq. (13) but also oxygen can escape which originally was present in the form of lattice ions. This assumption is self-evident if one considers that the established surface equilibrium

$$\mathrm{ZnO} \rightleftarrows \mathrm{Zn}^{\cdot}\ (\mathrm{ads}) + \mathrm{O}^{-}\ (\mathrm{ads}) \qquad (16)$$

will be shifted to the right due to the desorption according to Eq. (13), and the zinc oxide will be decomposed by photolysis. These combined reactions, (13) and (16), result in a large surface enrichment of donors and free electrons which can diffuse into the crystal (ambipolar diffusion). Zinc-metal precipitation can appear if the enrichment of donors and free electrons becomes so large that the chemical potential of the zinc-metal phase becomes substantial.

Further valuable information about the mechanism of the generation of charge carriers is obtained by experiments with zinc oxide doped with Li_2O and Ga_2O_3. Besides our own experiments, Trivich and co-workers (*18*) have investigated the photoconductivity of zinc oxide doped with Li_2O, Ga_2O_3, Al_2O_3, and CuO. These authors assume that the observed increase of the photoconductivity due to Li_2O doping is caused by the additional generation of free electrons due to the reaction

$$\mathrm{Zn}^{\cdot} + h\nu \rightarrow \mathrm{Zn}^{\cdot\cdot} + \mathrm{e}' \qquad (17)$$

This assumption seems to be reasonable with Li_2O-doped zinc oxide at longer wavelengths where an electron–hole formation in the valence band is not possible for energetic reasons. With pure zinc oxide, however, this mechanism should not play any decisive role because of the low concentration of donors. The same can probably be assumed for Li_2O-doped zinc oxide if the illumination occurs with light of 365 mμ where the electron–hole pair formation predominates.

If one considers that the incorporation of Li_2O

$$\mathrm{Li_2O} + \mathrm{e}' = 2\mathrm{Zn}|\mathrm{Li}|' + \mathrm{Zn}^{\cdot} + \mathrm{ZnO} \qquad (18)$$

causes a decrease of the concentration of free electrons and an increase of the donors ($\mathrm{Zn}|\mathrm{Li}|'$ denotes Li ion on zinc-ion lattice position) it becomes evident that practically no electrons are available for the chemisorption of oxygen. Therefore, the reaction of the electron–hole pairs with the chemisorbed oxygen cannot in this case be responsible for the increase of the photoconductivity during the illumination. We have to consider another mechanism for the reaction with the electron–hole pairs. It appears justified to assume tentatively a reaction of the electron–hole pairs with the donors in the following way:

$$\mathrm{Zn}^{\cdot} + |\mathrm{e}|^{\cdot} \sim \mathrm{e}' \rightarrow \mathrm{Zn}^{\cdot\cdot} + \mathrm{e}' \qquad (19)$$

$$\mathrm{Zn}^{\cdot\cdot} + \mathrm{e}' \rightarrow \mathrm{Zn}^{\cdot} \qquad (20)$$

Step (19) seems to be preferred except for the dark decay when reaction (20) predominates. In spite of the large concentration of free electrons produced during the illumination period, the participation of chemisorption of oxygen in the dark-decay period can be neglected, since O_2^- particles present at the surface would react with the doubly charged donors:

$$\mathrm{O_2}^{-}\ (\mathrm{ads}) + \mathrm{Zn}^{\cdot\cdot} = \mathrm{O_2}^{x}\ (\mathrm{ads}) + \mathrm{Zn}^{\cdot} \qquad (21)$$

By these considerations the observed faster rates of increase and decay of the photoconductivity of zinc oxide doped with Li_2O become understandable. While for pure zinc oxide the generation and destruction of charge carriers is determined by desorption and chemisorption, respectively, a process which takes time, the corresponding changes in the conductivity obtained with zinc oxide doped with Li_2O are faster because they are based only on electronic exchange processes without any chemical reactions.

To what extent the lithium ions in zinc oxide, $\mathrm{Li}|\mathrm{Zn}|'$, are more effective as traps for holes than the singly charged donors cannot be decided at present. In such a case the following mechanism would be conceivable

$$\mathrm{Li|Zn|'} + |\mathrm{e}|^{\cdot} \sim \mathrm{e'} \rightarrow \mathrm{Li|Zn|^{x}} + \mathrm{e'} \tag{22}$$

with the consequent reactions

$$\mathrm{Li|Zn|^{x}} + \mathrm{Zn}^{\cdot} = \mathrm{Li|Zn|'} + \mathrm{Zn}^{\cdot\cdot} \tag{23}$$

or

$$\mathrm{Li|Zn|^{x}} + \mathrm{e'} = \mathrm{Li|Zn|'} \tag{24}$$

For confirmation of this mechanism, however, further experiments are necessary.

A situation similar to that for pure zinc oxide seems to exist for the generation of charge carriers during illumination of zinc oxide doped with Ga_2O_3. According to the equation for the incorporation of gallium oxide:

$$\mathrm{Zn}^{\cdot} + \mathrm{Ga_2O_3} = 2\mathrm{Ga|Zn|}^{\cdot} + \mathrm{e'} + 3\mathrm{ZnO} \tag{25}$$

where $\mathrm{Ga|Zn|}^{\cdot}$ denotes a gallium ion on a zinc-ion lattice position, the concentration of donors here is strongly decreased and, correspondingly, the concentration of free electrons increased. Especially under these conditions an intensive chemisorption of oxygen occurs without surface reactions according to Eqs. (7) and (8) due to the absence of donors. The photoeffect, without doubt established on zinc oxide doped with Ga_2O_3, does not become effective because the concentration of free electrons in the dark has become so large, owing to the Ga_2O_3 doping, that the relative increase of charge carriers due to illumination is small. This condition is similar to that for pure zinc oxide annealed in high vacuum at high temperatures where the percentage increase of free electrons produced by illumination is also small due to the large initial concentration of electrons.

At present, it cannot be estimated to what extent the gallium ions in zinc-ion lattice positions can act as recombination centers for electron–hole pairs according to the following equations:

$$\mathrm{Ga|Zn|}^{\cdot} + \mathrm{e'} = \mathrm{Ga|Zn|^{x}} \tag{26}$$

$$\mathrm{Ga|Zn|^{x}} + \mathrm{e'} \sim |\mathrm{e}|^{\cdot} = \mathrm{Ga|Zn|}^{\cdot} + \mathrm{e'} \tag{27}$$

On the basis of the experimental results on the influence of carbon monoxide on the dark and photoconductivity of zinc oxide, a direct chemisorption of carbon monoxide on zinc oxide, with electron transfer to the catalyst, must be excluded. Due to the conductivity-decreasing influence of carbon monoxide on zinc oxide, both in the dark and in the illumination period, an uptake of carbon monoxide by zinc oxide is understandable only if it consists of a reaction with the chemisorbed oxygen. Besides the reaction of carbon monoxide with chemisorbed O^- particles

$$\mathrm{CO(gas)} + \mathrm{O^-(ads)} = \mathrm{CO_2^-(ads)} \tag{28}$$

the decrease of the dark- and photoconductivity forces us to assume a significant reaction with chemisorbed O_2^- particles. Therefore, the following reaction scheme can be tentatively proposed:

$$\mathrm{CO(gas)} + \mathrm{O_2^-(ads)} \rightarrow \mathrm{CO_2^-(ads)} + \mathrm{O^x(ads)} \tag{29}$$

with the subsequent fast reaction

$$\mathrm{O^x(ads)} + \mathrm{e'} \rightarrow \mathrm{O^-(ads)} \tag{30}$$

and reaction step (28). Only by such a mechanism are electrons consumed and therefore the conductivity must be decreased as found in the experimental results. Obviously, the presence of carbon monoxide with the simultaneous presence of oxygen in the gas phase or in a chemisorbed state causes a new steady state in the surface region of zinc oxide which is characterized by a smaller stationary concentration of free electrons both in the dark and during illumination. The CO_2 formation must play a decisive role, indeed, which is illustrated by the increase of the photoconductivity due to desorption of carbon dioxide upon illumination during evacuation (Fig. 10).

$$\mathrm{CO_2^-(ads)} \rightleftarrows \mathrm{CO_2(gas)} + \mathrm{e'} \tag{31}$$

The electron trapped by chemisorption is set free. The existence of chemisorbed CO_2^- particles at the zinc oxide surface was discovered by Schlosser and Hauffe (*19*) who measured the increase of the electrical resistance of zinc oxide by introduction of CO_2 into the gas atmosphere at various temperatures. These results are in agreement with those reported by Taylor and Amberg (*20*). These authors observed by means of infrared spectra in the region 2–9 μ that CO does not exist as such on the surface of zinc oxide at 155°C, but is immediately oxidized to CO_2. No evidence for carbonate formation in the adsorption of CO was detectable.

The results obtained in this paper are very important for the elucidation of the mechanism of the heterogeneous catalysis of the carbon monoxide oxidation both at dark and illuminated zinc oxide surfaces.

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