Photoproperties of Zinc Oxide with Ohmic and Blocking Contacts

by **H. J. Gerritsen, W. Ruppel** and **A. Rose.**

Laboratories RCA Ltd., Zurich, Switzerland.

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Abstract. Experiments on photo effects in fine grained zinc oxide layers are described. Primary as well as secondary photo currents were measured respectively with blocking and ohmic contacts. The primary photo current shows saturation with voltage and corresponds to a quantum yield close to unity.

The rise time of the secondary photo current is 10^4 times longer than that of the primary photo current, under an illumination that produces in both cases an equal density of free carriers. The reduced lifetime of the primary photo carriers in comparison with that for the secondary photo carriers and the assumption of equal trap density in both cases are sufficient to account for this effect. A trap density of $10^{14}/cm^3$ was obtained for the position of the Fermi level 0·8 eVolt below the conduction band and of $10^{17}/cm^3$ for the position of the Fermi level 0·4 eVolt below the conduction band. Both values apply to the traps in an energy slice kT around the Fermi level.

1. Introduction.

The photo conductive properties of ZnO have been studied extensively during the last ten years[1][2][3]. All of these measurements are typical for secondary photo effects and were carried out on semiconducting samples. The measurements reported in this paper were done on relatively insulating ZnO and show that the same material can exhibit both secondary and primary photo currents. The secondary photo effect is obtained with ohmic contacts, here metal electrodes, while the primary photo effect is obtained when one of the electrodes is blocking. All the criteria for a primary photo current[4] were observed, i.e. saturation with increasing voltage, unity quantum yield and relatively short rise time. It has been pointed out by one of us[5] that the rise time for the primary photo current can be slowed down by traps and need not necessarily be as short as 10^{-4} seconds, as suggested by GUDDEN and POHL[4]. The experiments indeed confirm this idea.

In addition to reversible secondary and primary photo effects, irreversible photo effects have also been observed when strong illumination was applied for a long time.

For "pure" zinc oxide the quantum yield was observed to drop rapidly when the wavelength was increased from the strongly absorbed ultra violet into the visible region. For dye sensitized zinc oxide*) a high quantum yield is maintained over a large part of the visible region.

2. Experimental techniques.

The surface potential was measured with a transparent conducting probe electrode close to the surface and connected to an electrometer. The transparent electrode allowed measurements of the surface potential to be made under illumination. The absolute intensity of the illumination was measured with a set of calibrated RCA photocells, 919, 929 and 935, covering the spectrum from the red into the ultra violet. Interference filters in front of an incandescent lamp served as a source for monochromatic light.

In some experiments the transparent electrode was connected to ground through a microammeter. The current that flows in the charged zinc oxide layer when it is illuminated induces a current to flow through the microammeter, proportional to the photo current.

In the measurements of photo current along the surface, the secondary photo current, electrodes were pressed on the surface of the zinc oxide layer, close to each other. A voltage was applied between them and the current along the surface was measured under illumination.

3. Experimental Results.

The zinc oxide on which the experiments were done consisted of a powder with a particle size of about 10^{-5} cm, embedded in some plastic. In the results to be described here, a silicone plastic was used and the layers were about 20 μ thick, but it was observed that the nature of the plastic was not critical for the results. The role of the plastic is discussed in more detail in the preceding paper.

A. *Primary photo effect.*

All the experiments to be described below were performed on zinc oxide layers, stored for a long time in the dark. It was observed that very strong illumination produced changes in the conductivity of the zinc oxide that disappeared only partially in the course of some days.

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*) The dye sensitized material was developed by C. J. YOUNG and H. G. GREIG and is described in RCA Rev. **15**, 469 (1954).

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A zinc oxide layer, was charged with a negative corona up to a surface potential of about − 500 V. This voltage decays very slowly, in about a day, so that ample time for measurements is available. The following experiments were done:

a) *Saturated current.* The current that flows in the layer together with the surface potential were measured during illumination as a function of time for two different light intensities. The results are
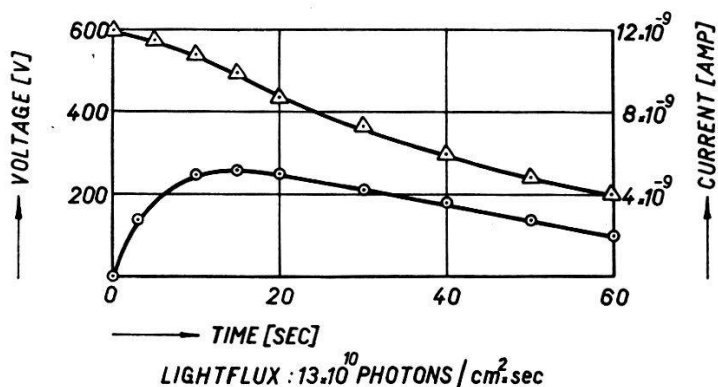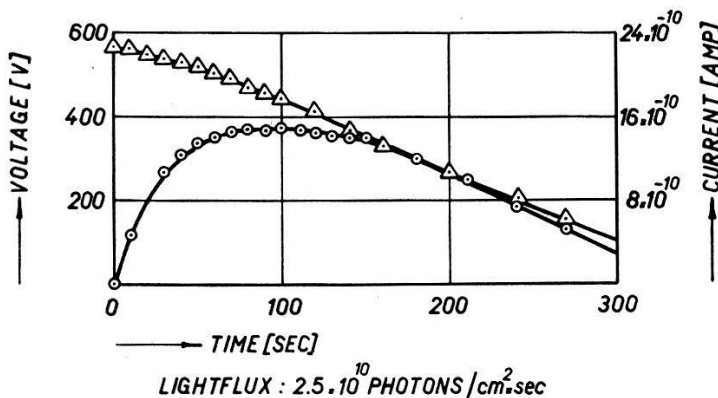
FIG. 1a.

LIGHTFLUX : $13 \cdot 10^{10}$ PHOTONS / $cm^2 \cdot sec$

FIG. 1b.

LIGHTFLUX : $2.5 \cdot 10^{10}$ PHOTONS / $cm^2 \cdot sec$

△ VOLTAGE MEASUREMENTS
⊙ CURRENT MEASUREMENTS

Fig. 1a and 1b.
Primary photo current and surface potential of a charged zinc oxide layer under illumination.

plotted in figure 1a and 1b. The light used was UV radiation of 3680 Å, which is strongly absorbed by the zinc oxide in accordance with the band gap of 3.2 eV.

In the figures one sees that the current is approximately constant when the voltage is between 500 and 350 V. Because of the interfering effect of the relatively long rise time for the photo current, one can not conclude with certainty that the current is saturated in that voltage range. The saturation is better borne out by the following experiment.

A zinc oxide layer was charged by corona, its surface potential was measured; and subsequently it was exposed to a short light flash. After the flash the surface potential was measured again. If one assumes that the capacity of the layer is a constant, the observed
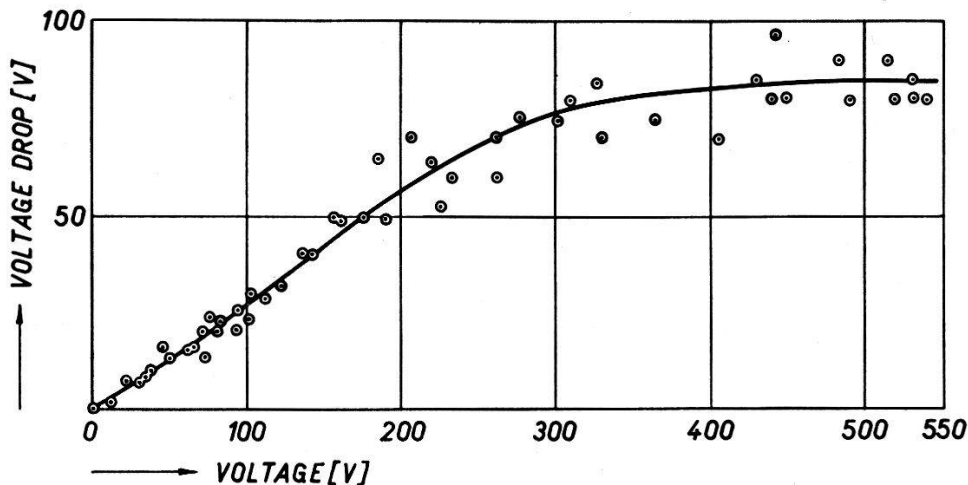

Fig. 2.

Voltage drop vs. initial voltage for a light flash of 7×10^{11} photons/cm² of 3680 Å.

voltage drop should be proportional to the charge that has flowed through the layer. The voltage drop was studied as a function of initial surface potential and the result is plotted in Figure 2. The range of values for the initial surface potential were obtained by
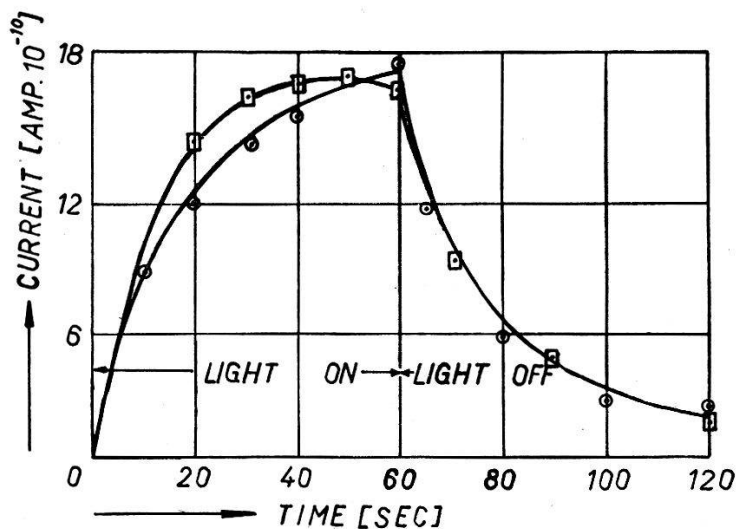
Fig. 3.

Rise and decay time of the primary photo current for two different initial voltages.

allowing the charged layer to decay in the dark for various times before carrying out the experiment. It was ascertained in a separate experiment that the surface potential continued to drop rather rapidly in the first moments after the illumination had stopped, so

that a time lapse was taken, between the illumination and the measurement of the surface potential, sufficiently long for the complete decay of the photo current to take place. The experiment shows clearly that the transported charge is not dependent on voltage above about 300 V.

In Figure 3 several representative current vs. time curves are given for different initial voltages for a flash of light. What is to be noted is the essential invariance with voltage of the set of curves. The finite rise and decay times point to trapping effects.

b) *Quantum yield.* The quantum yield, defined as the number of electron charges transported through the layer per incident photon, was measured in the region above 300 V. The condensor relation:

$$\Delta Q = \frac{\varepsilon_0 \, \varepsilon \, \Delta V}{4 \, \pi \, d}$$

with a measured dielectric constant of 8 and $d = 2 \cdot 10^{-3}$ cm was used to calculate the number of electrons discharged per cm² for a measured voltage drop ΔV. The number of photons incident per cm² was obtained from the product of exposure time and light intensity. The quantum yield has been plotted as a function of wavelength in Figure 4. The high quantum yield of 0·25 occurs at 3680 Å, where the zinc oxide absorbs strongly, while little effect is observed for radiation with wavelength longer than that corresponding to the band edge of the absorption curve. No correction has been made for scattering and reflection of the light, which may change the values for the quantum yield by a factor of as much as 4.

An experiment was done in order to decide whether short intense exposures caused a voltage drop different from prolonged weak exposures, with the same total number of incident photons. The result was that the same quantum yield was obtained for exposure times between 100 and 10^{-2} seconds. The accuracy was such that a change of a factor of 2 would have been detected.

The quantum yield for a layer of zinc oxide to which some fluorescein dye had been added is given in Figure 4 and shows the effect of "sensitization" in the visible region.

c) *Sign of photo excited charge carriers.* The normal procedure was to discharge a negatively charged layer with UV light incident at the negatively charged surface. Because the absorption coefficient of zinc oxide single crystals[6] in the UV is 3×10^5 cm⁻¹, the holes have to move only about 0·03 μ to reach the negatively charged

surface, while the electrons must move 20 μ in order to reach the positive charge at the grounded backside of the layer.

An experiment was done in which the zinc oxide layer was deposited on a transparent conducting backing, so that light could now also be directed at the positively charged side of the layer. It turned out that this side needed about 30 times longer exposure for the same voltage drop as was obtained for light directed at the negatively charged side. It is probable that a large fraction of the

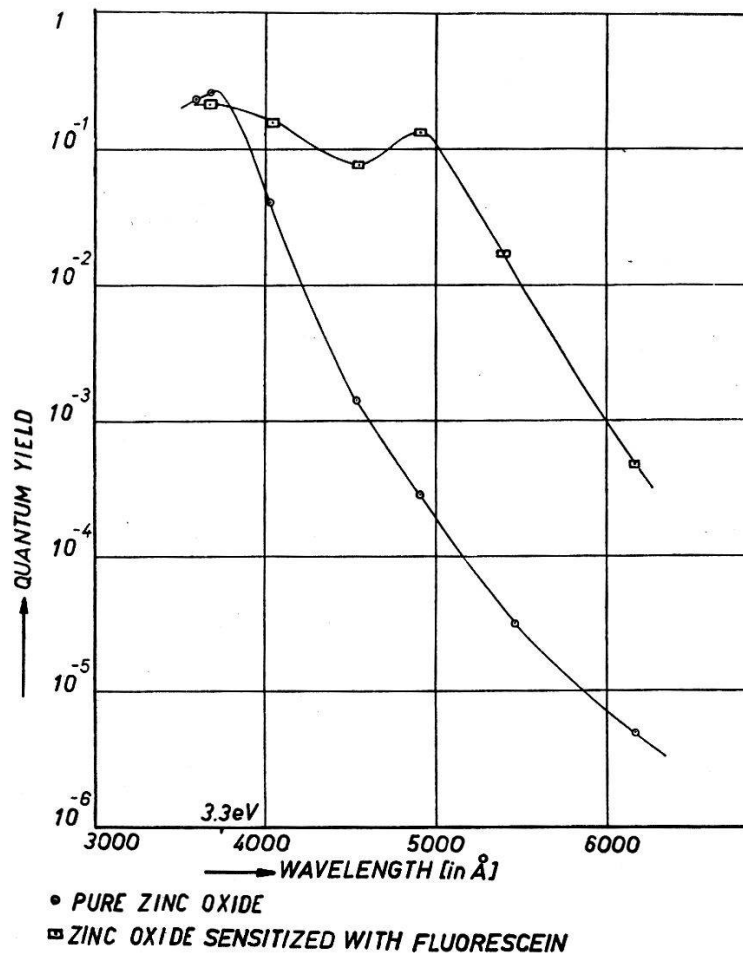● PURE ZINC OXIDE
▣ ZINC OXIDE SENSITIZED WITH FLUORESCEIN

Fig. 4.
Quantum yield in zinc oxide for different wavelengths.

residual sensitivity is due to light that reaches the negatively charged surface by scattering effects inside the layer and between the grains. In a separate test it was observed that the layers showed a transmission of 2% for UV radiation. The fact that light to be effective in discharging must be absorbed at the negatively charged side of the zinc oxide layer leads thus immediately to the conclusion that the mobile photo excited carriers are electrons in accordance with expectation.

B. *Secondary photo effect.*

a) *Gain and lifetime determinations.* When metallic electrodes are placed on the zinc oxide layer, close to each other, a photo current is obtained under illumination which flows parallel to the surface and shows the behaviour typical for a secondary photo effect. It was observed that after a rise time of minutes to hours, depending upon light intensity, the steady photo current can be represented by the relation:

$i_{ph}/e = GF$, where i_{ph} = photocurrent, G = Gain = number of electron charges passed through the photoconductor per incident photon per second and F = number of photons that strike the surface between the electrodes per second. The gain is the ratio of lifetime, τ, to transit time T_r, where $T_r = L^2/\mu$ V. L is the distance between electrodes, μ is the mobility and V the voltage between the electrodes. Gains far in excess of unity were obtained by placing the electrodes close to each other and using a high voltage between them. From this gain, a lifetime was obtained of $\tau = 10^{-4}$ seconds, assuming a mobility of unity*). This time is the time a photo excited electron spends in the conduction band before it recombines with a hole.

C. *Rise time of primary and secondary photo currents.*

The rise times of primary and secondary photo currents were compared under illuminations that produced in both cases the same free carrier density. In order to do that, the UV light flux for the primary case was 7×10^{11} photons/cm² sec while for the secondary case it was about four orders of magnitude smaller. The free carrier density in the primary case was calculated from the observed current density, assuming a mobility of unity. In the same way a density of 6×10^5 electrons/cm³ was computed for the secondary current assuming that the current was confined to a layer about 10^{-5} cm thick corresponding to the depth of penetration of the light.

The rise time observed for the primary effect equals 1 second and for the secondary effect 10^4 seconds. If no trapping were present, both rise times would be equal to the appropriate life times, namely 10^{-8} seconds (transit time = life time in primary effect) and 10^{-4} seconds respectively.

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*) Mobilities as high as 200 cm²/Vsec are observed for pure single crystals[7]. Sintered layers, however, show mobilities of the order of 10 cm²/Vsec. For the powdered layers, a value of unity is not unreasonable.

For trapping the following relation holds [6]:

$$\tau_0 = \tau_l \frac{n_{tr}}{n_f} \text{, where}$$

τ_0 = rise time of photocurrent.
τ_l = life time of free carrier.
n_f = number of free electrons per cm³.
n_{tr} = number of trapped electrons per cm³ in the neighbourhood of the Fermi level. Apparently both primary and secondary effects lead to a value of 10^{14}/cm³ for n_{tr}. The position of the Fermi level, deduced from the number of free electrons was 0·8 eV below the conduction band. A similar measurement of the rise time of the secondary photo effect under strong illumination led to a trap density of 10^{17}/cm³ at the Fermi level 0·4 eV below the conduction band.

4. Summary and Discussion.

The fact that oxygen ions deposited by the corona make a blocking contact with the zinc oxide, but that metallic contacts make an ohmic contact has been discussed in the foregoing paper. In the present paper it is shown experimentally, that the photo effect for a blocking contact is a primary one and for the ohmic contact a secondary one.

The rise time of the primary current is 10^4 times faster than the secondary current and is consistent with the free carrier life time for the primary current being smaller than that for the secondary current by the same factor. For both primary and secondary currents the observed rise times are about 10^8 times larger than their respective free carrier life times. Both rise times are accounted for by the same ratio of trapped to free carriers. A trap density of 10^{14}/cm³ is deduced for an energy slice kT wide at 0·8 eV below the conduction band.

No evidence for the motion of holes greater than 10^{-5} cm was found. An extremely short hole life time is to be expected in a photoconductor sensitized to have a relatively long life for free electrons.

The effect of dye sensitization is also observed in the silver halide process[8] and in CdS[9], where it is ascribed to electrons excited from levels due to the dye.

As far as the photo properties of the zinc oxide powder-plastic layers are concerned, the layer can be treated essentially as a homogeneous layer of zinc oxide. Neither the particle nature of the zinc

oxide nor the presence of the plastic enter explicitly into the understanding of the photo currents.

In this paper, as in the foregoing one, the writers are indebted to C. J. Young*), H. G. Greig*), and J. A. Amick*) for their many contributions and helpful discussions.

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*) RCA Laboratories, Princeton, New Jersey.