

Photoconduction and Surface Effects with Zinc Oxide Crystals

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Large photoconductive effects have been observed on single crystals of ZnO at 300°K and 78°K. At 300°K the decay of the photoconductivity is strongly dependent on the ambient conditions, being slow in vacuum and fast in wet oxygen. This shows that the conductivity is associated with the surface. The effects are essentially independent of the dark conductivity of the crystals and cannot be accounted for by the desorption of adsorbed oxygen. It is proposed that holes from hole electron pairs discharge lattice oxygen ions at the surface, producing a surface excess of zinc and an electron enrichment layer in which conduction occurs. The formation of this layer has been followed as a function of the total number of photons incident on the crystal. In the initial stages quantum efficiencies as high as 0.25 have been observed for this process.

INTRODUCTION

THE importance of the surface in controlling the semiconducting properties of zinc oxide has been known for many years. Studying the photoconductivity of evaporated films of zinc oxide, Mollwo¹ and his group in Germany found that the rate of increase of conductance on illumination as well as the rate of decay after illumination depended on the ambient oxygen pressure. In fact the decay in high vacuum was so slow that the effect could be considered irreversible. In addition to the "slow" irreversible effect a reversible "fast" component of the photoconductance was observed. In this country Miller^{2,3} and co-workers studied the behavior of sintered layers of zinc oxide and observed the slow effect and its dependence on the ambient oxygen pressure but were not able to distinguish a fast effect. The slow effect in both cases was attributed to the desorption and readsorption of oxygen. In the dark the adsorbed oxygen atom becomes negatively charged by the capture of an electron, thereby creating a depletion layer of low conductivity near the surface. The destruction of the depletion layer and the consequent increase in conductance results from the desorption of the adsorbed oxygen layer. This may be accomplished when the holes produced by light absorbed near the surface discharge the oxygen ions. The magnitude of the changes in conductance to be expected from the adsorption and desorption of the oxygen layer can be calculated,⁴ if the geometry and donor density are known; however, such a calculation cannot be carried out for sintered layers.

Recently, in needle-like single crystals of ZnO where the surface-to-bulk ratio is smaller than that of sintered material, surface effects have been found to affect the

conductance drastically. Heiland⁵ has reported that atomic hydrogen produces a surface conductivity corresponding to a surface donor concentration of nearly 10^{13} ions/cm². The conductivity is known to be at the surface because oxygen destroys it at room temperature when diffusion into the bulk is negligible. A somewhat smaller but apparently different surface conductivity is produced by heating to 527°C in 5 atmospheres of hydrogen. By exposing crystals to zinc vapor at a temperature at which no diffusion into the crystal occurred, Thomas and Lander⁶ showed that adsorbed zinc atoms act as donors at the surface, giving up electrons to the crystal. Surface concentrations approaching 10^{13} ions/cm² were obtained. It seems probable that hydrogen, which gives a conductive surface above 250°C, reduces the crystal surface to give zinc atoms. It may be that atomic hydrogen reacts similarly at room temperature.

Mollwo¹ reported that no photoconductivity could be detected with single crystals at room temperature, perhaps because the crystals were too conductive to allow observation of the small changes brought about by light. At 90°K when the crystals are normally of low conductivity either because the donors are no longer completely ionized or the electrons are trapped, Heiland⁷ observed photoconductivity. He described a fast reversible effect as well as a slow permanent effect which was connected with the loss of oxygen.

The work with single crystals in which the surface area can be defined has shown not only that the surface may be negatively charged due to adsorbed oxygen atoms acting as surface acceptors but may be positively charged by the action of surface donors. A negative charge at the surface causes the conduction band near the surface to bend upward away from the Fermi level and in an *n*-type semiconductor, such as ZnO, reduces the electron concentration. Such a region is called a depletion layer. On the other hand, a positive charge on the surface bends the conduction band down toward the Fermi level and for ZnO increases the electron

¹ E. Mollwo, in *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 509.

² P. H. Miller, in *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 287; S. R. Morrison, in *Advances in Catalysis* (Academic Press, Inc., New York, 1955), Vol. 7, p. 259.

³ D. A. Melnick, *J. Chem. Phys.* 26, 1136 (1957).

⁴ G. Heiland, *Z. Physik* 138, 459 (1954); H. J. Krusemeyer and D. G. Thomas, *J. Phys. Chem. Solids* 4, 78 (1958).

⁵ G. Heiland, *Z. Physik* 148, 15 (1957); 148, 28 (1957).

⁶ D. G. Thomas and J. J. Lander, *J. Phys. Chem. Solids* 2, 318 (1957).

⁷ G. Heiland, *Z. Physik* 142, 415 (1955).

concentration producing an enrichment space-charge layer. In the latter case the high density of states in the conduction band allows a high concentration of electrons in the surface layer without a prohibitively large voltage drop across the layer.

In this paper we shall describe the photoconductivity of single crystals mostly at room temperature. It will be shown that the behavior is dominated by the formation of the enrichment-type space-charge layer arising from a photolysis of the surface of the zinc oxide lattice. The photolysis can occur when the holes, from hole-electron pairs generated by light, discharge surface lattice oxygen ions leaving an excess of zinc at the surface. The conductivity so produced is similar to that resulting from the adsorption of zinc atoms from the vapor.

EXPERIMENTAL

Colorless hexagonal crystals, about 0.5 cm long and 7×10^{-3} to 2.5×10^{-2} cm in diameter, were grown in this laboratory by the method of Scharowsky.⁸ Out of about 100 lots grown, the crystals in several lots had room temperature conductivities less than 10^{-2} (ohm cm)⁻¹; the conductivity increased only slightly on heating and decreased sharply on cooling. Because of their low conductivity these crystals were used in their original state, and were also used for those experiments involving crystals doped with interstitial zinc according to the technique described by Thomas.⁹ Crystals of extremely low conductivity [about 10^{-7} (ohm cm)⁻¹] were produced by doping with lithium which, in a substitutional lattice position, acts as an acceptor. The crystals were doped by allowing a layer of strong lithium hydroxide solution to dry on the crystal surface, followed by heating in air to 700°C for an hour. In order to restore the surface sensitivity after this treatment, it is necessary to etch the surface for about $\frac{1}{2}$ hour in 10% HF. Contacts were made to the ends of the crystals by wetting with gallium and were ohmic and relatively noise-free.

The crystal conductivities were measured, as shown in Fig. 1, by observing the voltage across the load resistor R_L in series with the crystal and a battery. By shadowing the contact area and observing that the effect changed only by an amount to be expected from the fraction of the crystal shadowed, it was shown that the photoconductivity was not associated with the contacts. One end of the crystal was held in a copper block and the other end in a flexible wire in thermal but not electrical contact with the copper. The copper block was in a metal Dewar with two quartz windows, and could be cooled with liquid nitrogen. In the work involving temperature cycling, four contacts were made to the crystals which were suspended in a quartz tube, and a mercury arc was held nearby for a time long enough to give the desired conductivity level.

⁸ E. Scharowsky, *Z. Physik* **135**, 318 (1953).

⁹ D. G. Thomas, *J. Phys. Chem. Solids* (to be published).

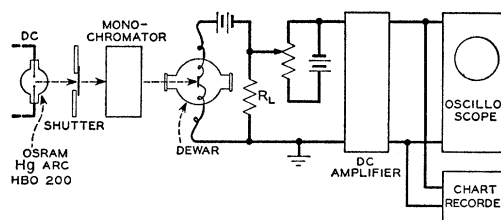


Fig. 1. Experimental apparatus used to study the photoconductivity of zinc oxide.

Usually the crystals were illuminated with monochromatic light of known intensity obtained from a high-pressure dc Hg arc (Osram HBO 200) and a Model 99 Perkins Elmer Monochromator. A slit width of 5×10^{-2} cm was used which was wider than the crystals, so that when the crystals were placed at an image of the exit slit they were completely illuminated on one side. As measurements were always made on a line of the mercury spectrum, scattered radiation of other wavelengths could be neglected. When necessary the intensity of the light was reduced by placing wire gauzes at a field plane in the focusing optics before the monochromator. The absolute energy incident on the sample was measured with a thermocouple which had been calibrated against a National Bureau of Standards standard lamp and is accurate to better than 50%. A standard photographic shutter provided a convenient means of obtaining variable-length light pulses and at the same time a synchronizing pulse for the oscilloscope. The results of the short pulses were photographed from the oscilloscope trace and longer pulses were displayed on a pen recorder.

RESULTS

Wavelength Dependence

The first experiments determined the wavelength dependence of the photoconductivity at room temperature in air. Light was chopped at 13 cycles/second and the signal from the crystal was detected with a phase-sensitive amplifier. The response decayed quite rapidly if the chopped light was kept on continuously and so experiments of short duration were made at different wavelengths. The results are shown in Fig. 2. The onset of photoconductance coincides with the onset of the fundamental optical absorption edge, i.e., the absorption due to the excitation of an electron from the valence to the conduction band. At wavelengths between about 0.4 and 4.0 microns (i.e., 3.1 and 0.31 eV) no response could be seen at room temperature; at 78°K weak response was noted at 1.0 micron (1.2 eV) and at 3 micron (0.4 eV). At 78°K the onset of the photoconductance in the fundamental shifted to shorter wavelengths and the response in the region of the absorption threshold showed several maxima and minima.

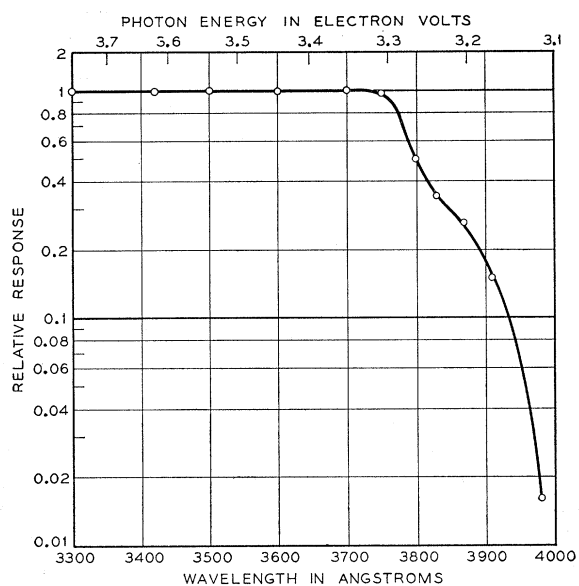


FIG. 2. Relative photoconductive response at 13 cps to short exposures of radiation, as a function of wavelength.

Rise and Decay of Photoconductivity

Light absorbed in the fundamental absorption band produced an effect which, in the presence of oxygen, decayed in the order of minutes, and therefore was not simply the production and decay of mobile holes and electrons which we may term a "fast effect." Furthermore, most, if not all, of the photoconductivity was associated with the crystal surface. The conductivity of crystal 24L, which was 1.6×10^{-2} cm in diameter and had a dark conductivity σ_d of 5×10^{-4} (ohm cm) $^{-1}$, is plotted in Fig. 3 as a function of time in both oxygen and nitrogen. On illumination in nitrogen there is an increase

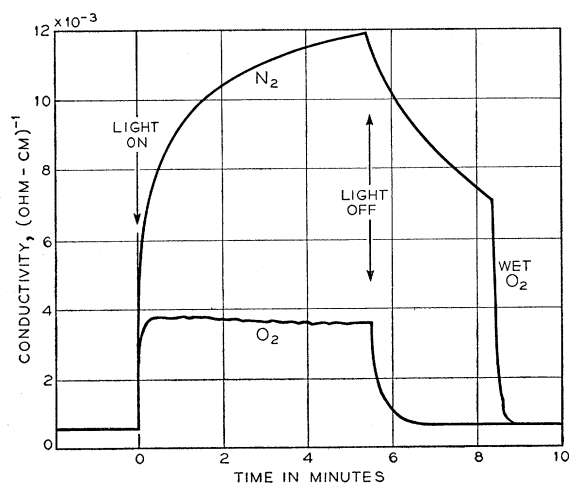


FIG. 3. The photoconductivity of ZnO single crystal 24L in 1 atm of O_2 and N_2 at $25^\circ C$ when illuminated with $170 \mu w/cm^2$ of 3131 Å radiation. Diameter of crystal = 0.016 cm. Admitting wet O_2 to the system rapidly restored the initial conductivity.

over the initial dark conductivity of more than a factor of 10, and in oxygen there is a smaller increase. The dependence of the rate and magnitude of the change in conductivity on the ambient conditions clearly indicates the importance of surface effects. Further confirmation comes from the rapid destruction of the added conductance when wet oxygen is admitted to the system (breathing on the samples is very effective in this respect). The effect may be repeated as often as desired. If the crystals are illuminated in a vacuum, the rise is similar in magnitude to that for nitrogen and the decay is very slow. In pressures of about 10^{-6} mm many hours are required for the current to decay to 10% of its original value.

Temperature Variations of Added Conductivity

The temperature dependence in vacuum of the conductivity produced by light for a crystal [$\sigma_d = 2 \times 10^{-8}$ (ohm cm) $^{-1}$] is given in Fig. 4. It should be emphasized

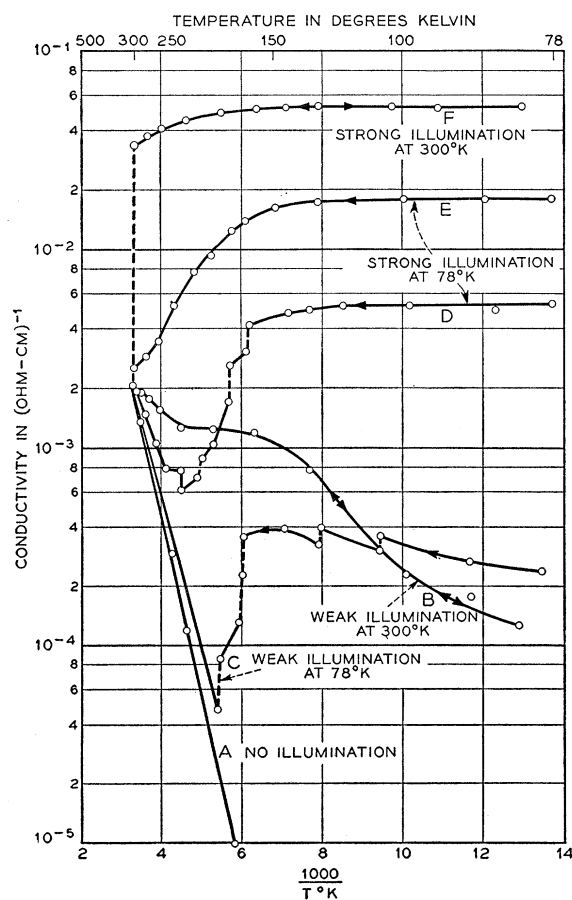


FIG. 4. Conductivity measured in the dark of crystal 24F (1.5×10^{-2} cm diameter) as a function of temperature after the following treatment: Curve A—no illumination; Curve B—weak illumination at $300^\circ K$; Curve F—strong illumination at $300^\circ K$; Curve C—weak illumination at $78^\circ K$; Curves D and E—stronger illumination at $78^\circ K$ for different durations.

that these curves are all taken in the dark. Curve *A* shows how the dark conductivity decreases with decreasing temperature. Illumination at 78°K can produce curves such as *C*, *D*, or *E* depending on how much light had fallen on the crystal. After illumination at 78°K the conductivity can be cycled reversibly between 78°K and 170°K, but above this point decay begins even at constant temperature until curve *A* is regained. The behavior is different if the crystal is illuminated at room temperature. Curves *F* and *B* result from illumination at 300°K and are reversible for cycling between 300°K and 78°K. Similar curves have been reported by Weiss¹⁰ for sintered ZnO.

Absence of "Fast Effect"

No rapid initial rise or decay of the photoconductivity was observed in our experiments, although the effect was followed on an oscilloscope over a wide range of light intensity and length of exposure. For undoped crystals restored to their dark conductivity, the first part of the curve rises linearly with time before becoming nonlinear and approaching saturation, as shown in Figs. 5(a), (b), and (c); 5(a) shows the nonlinear rise at high intensity over a long time, 5(b) with a weaker light and a short pulse shows the linear region for part of the flash, and 5(c) with a very weak light and a short pulse shows the linear rise for the whole flash. The designation of the vertical scale in electrons/cm² cm will be explained below. The absence of a "fast" component of decay is also evident from these figures. The effect produced by a small number of photons being incident on the crystal, as in 5(c), does decay over a period of several seconds even in a high vacuum, whereas larger increases in conductivity decay much more slowly under these conditions.

Buildup of Photoconductance

The over-all buildup of the effect was measured by taking a series of flashes each 10 times as long as the previous one, allowing most of the effect to decay after each flash. (In vacuum the decay was not complete, but the effect produced by the next flash was always large compared to that from the last.) This was done for light of different intensities and under different ambient conditions. Figure 6 shows the results for crystal *K-1* [$\sigma_d = 3 \times 10^{-3}$ (ohm cm)⁻¹] in vacuum at room temperature; the electrons produced per square centimeter are plotted as a function of the photon/cm² incident on the crystal surface. If the additional electrons are assumed to move in a space-charge layer near the illuminated surface with a mobility of 100 cm²/v sec,¹¹ the number of conduction electrons/cm² (N_e) is related to the observed conductance change (Δg) by

$$N_e = (l^2 / A e \mu) \Delta g, \quad (1)$$

¹⁰ H. Weiss, Z. Physik **132**, 335 (1952).

¹¹ H. J. Krusemeyer, Bull. Am. Phys. Soc. Ser. II, **3**, 217 (1958).

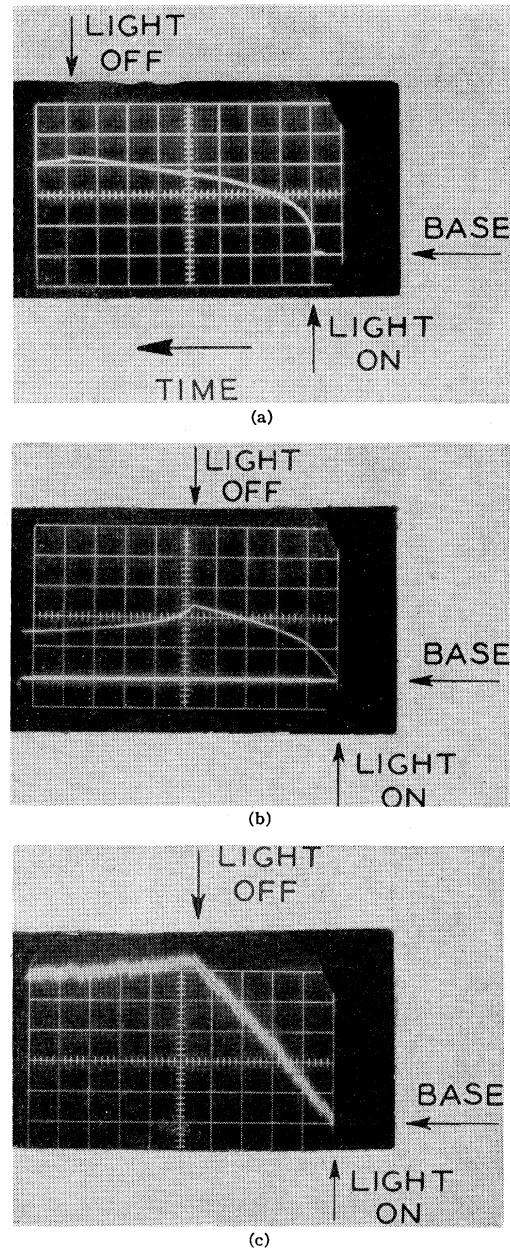


Fig. 5. Room-temperature photoconductivity of crystal 24L in N₂ at 3131 Å. (a) 5.2×10^{14} photons/cm² sec. Vert., 500 mv/cm $\equiv 7.5 \times 10^{11}$ electrons/cm² cm. Horiz., 2 sec/cm. (b) 6.6×10^{12} photons/cm² sec. Vert., 10 mv/cm $\equiv 1.5 \times 10^{10}$ electrons/cm² cm. Horiz., 20 msec/cm. (c) 1.65×10^{11} photons/cm² sec. Vert., 0.1 mv/cm $\equiv 1.5 \times 10^8$ electrons/cm² cm. Horiz., 20 msec/cm.

where l = distance between electrodes, A = area of sample illuminated, e = electronic charge, and μ = mobility. A quantum efficiency (electrons per photon) of 0.25 is observed for the initial linear region. For sample *K-1*, after about 2×10^{10} electrons/cm² have been produced, the quantum efficiency steadily falls off until saturation is approached near 10^{13} electrons/cm². In vacuum the number of conduction electrons produced

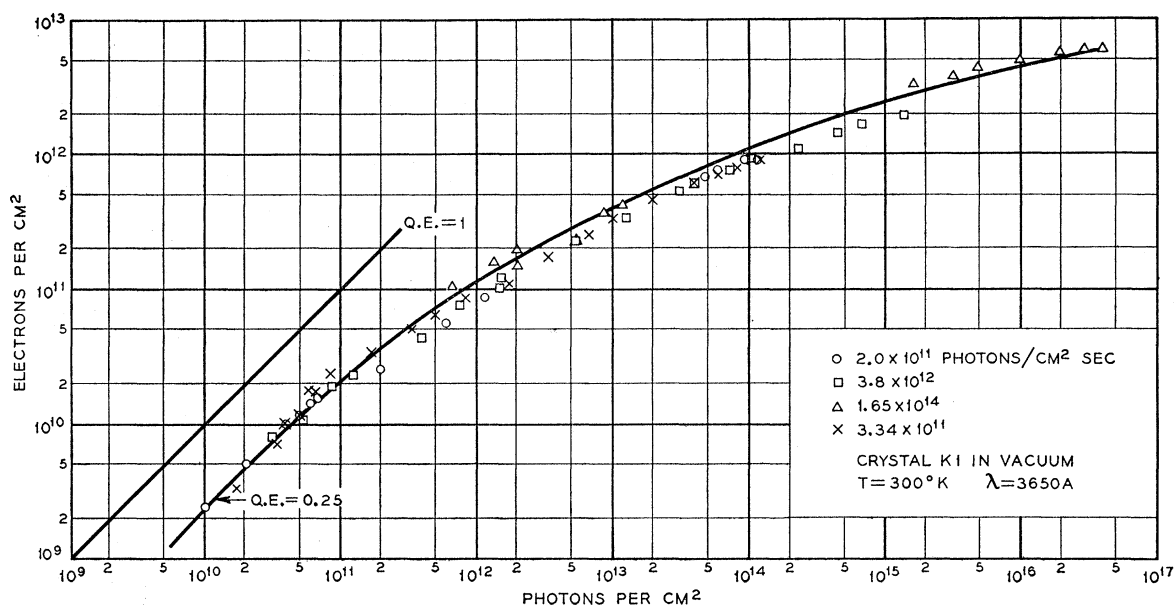


FIG. 6. Number of surface conduction electrons/cm² produced as a function of integrated number of incident photons/cm² at various light levels for crystal *K-1* [$\sigma_d = 3 \times 10^{-3}$ (ohm cm)⁻¹]. An electron mobility of 100 cm² per volt second has been assumed in Eq. (1).

can be seen (Fig. 6) to display reciprocity between time and radiation density. This experiment has been carried out with several crystals, with similar results.

In oxygen a curve similar to the vacuum condition curve is followed below about 10^{11} electrons/cm². Above this level the curve falls below the vacuum curve and definite saturation values are reached. Figure 7 shows saturation values of the surface conductivity of crystal *P5* ($\sigma_d = 6 \times 10^{-3}$ ohm⁻¹ cm⁻¹) in air, for light of various intensities and for various wavelengths in the fundamental absorption region. The conductivity produced by a certain photon intensity is roughly the same for photon energies between 3.96 and 3.40 eV.

Illumination at Low Temperature

As mentioned above, illumination of the crystal at 78°K also results in an increase of conductivity which

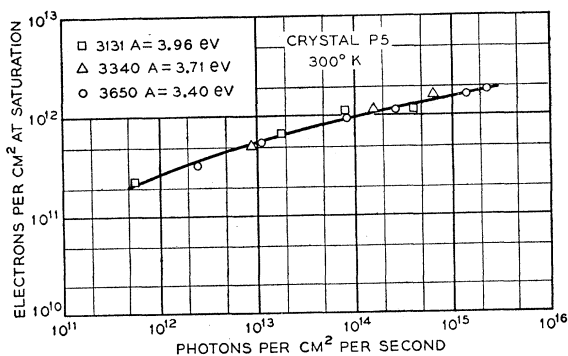


FIG. 7. Saturation surface photoconductivity in air vs light intensity for different wavelengths at room temperature.

persists long after the light has been extinguished; the magnitude of the effect is about the same as that at room temperature. However, not until 10^{13} to 10^{14} photons/cm² were incident on the surface were appreciable changes apparent, after which a more normal increase of conductance occurred. Although the details of the low-temperature process are not understood, we believe the phenomena is essentially the same as at 300°K. At low temperatures the crystals have a high resistivity, probably because of electron traps, and these traps would have to be filled by electrons produced by the light before an increase in conductance could be observed. The fact that the conductivity produced at low temperatures decays on warming will be discuss below.

Photoconductivity of Crystals of Different Dark Conductivities

Crystal *24L* was doped with interstitial zinc so that its conductivity was raised from 0.001 to 0.1 (ohm cm)⁻¹. The percentage change in conductance produced by light is now much smaller but it is still subject to the effects of oxygen. After the interstitial zinc is removed and the sample is given a light etch, the behavior of the untreated crystal is restored. Although the measurements do not go to very low values of surface conduction electron concentration because of the difficulty of observation on the doped crystal, Fig. 8 shows the result with the crystal in three conditions. The lack of dependence of the surface effect on the bulk conductivity is clearly seen.

Crystals doped with substitutional lithium have low conductivities and as a result the photoconductivity is a large percentage effect. That the presence of the

lithium does not limit the over-all conductivity increase which may be observed, provided the surface has been etched after doping. Figure 9 shows the buildup of photoconductivity for crystal 23L after doping with lithium. No region of constant quantum efficiency is observed and the initial quantum efficiency is rather low, about 0.015. This curve again illustrates the reciprocity, particularly in vacuum, between time of exposure and intensity of light. Except at the highest levels of surface conductance, the same total number of photons produces the same effect independent of the rate of arrival of photons. As usual the rate of decay is strongly dependent on the ambient conditions, and wet oxygen can cause an almost instantaneous decrease of apparent crystal conductivity by at least a factor of 10^4 .

A close study of the decay rate has not been made. It depends on the pressure of the surrounding oxygen and the humidity, and if these factors are held constant it is still not a simple function of the excess photoconductivity but depends on the history of the sample. The rate appears to be greater for freshly etched surfaces than for aged surfaces.

The results which we have quoted are quite reproducible and are very similar from one crystal to another whether the crystal is doped or undoped, of high or low resistivity. However, certain treatments do affect the surface and thereby reduce or alter the photoconductive effect. For example, after the interstitial zinc is removed from a doped crystal by heating at 500–600°C in air for a few minutes, the surface is not very sensitive to light. Etching the sample for a minute

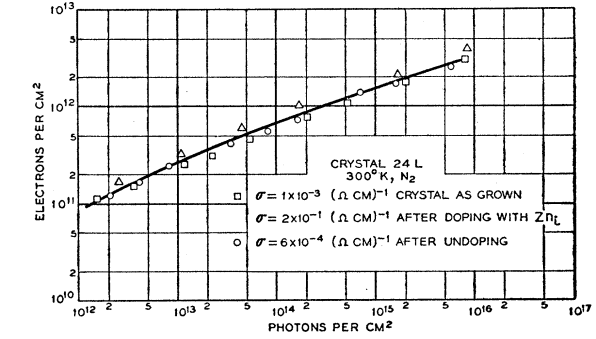


FIG. 8. Number of surface conduction electrons/cm² produced as a function of integrated number of incident photons/cm² for a single crystal in three conditions of doping: as grown [$\sigma_d=1 \times 10^{-3}$ (ohm cm)⁻¹], doped with interstitial zinc [$\sigma_d=2 \times 10^{-1}$ (ohm cm)⁻¹], and after removal of the interstitial zinc [$\sigma_d=6 \times 10^{-4}$ (ohm cm)⁻¹].

in dilute nitric acid restores the “normal” behavior. As much as 0.001 in. has been etched off crystals and the surface effects persist.

DISCUSSION

It is believed that the largest contribution to the photoconductivity just described arises from the formation of an enrichment-type space-charge layer with donor atoms at the surface, rather than the destruction of a depletion layer by light as has often been supposed in the past. The following example shows that the changes in conductance predicted by the depletion-layer model are too small to account for the present observations. Under illumination, crystals with

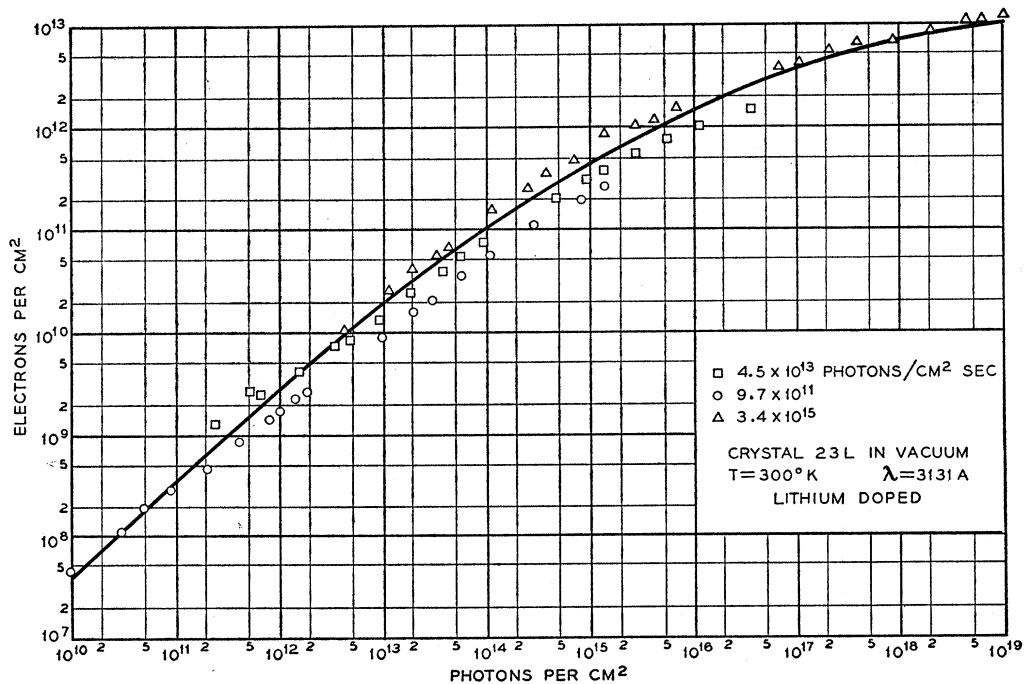


FIG. 9. Number of surface conduction electrons/cm² produced as a function of integrated number of incident photons/cm² on a crystal doped with substitutional Li to reduce the dark conductivity to 10^{-7} (ohm cm)⁻¹. Electron mobility was assumed to be 100 cm²/volt sec.

a diameter of 2×10^{-2} cm can acquire an apparent additional conductivity of approximately 0.01 (ohm cm^{-1}). Figure 3 shows such a case, and shows too that in the dark the crystal conductivity is at least 10 times less than 0.01 (ohm cm^{-1}). For the case in which the surface is more than $2(kT/e)$ volts negative with respect to the center of the crystal and all the bulk donors are ionized, Krusemeyer and Thomas⁴ have given the formula in the mks system of units for the negative-charge concentration at the surface, m^- :

$$m^- = \left[\frac{2kTn_{\infty}^- \epsilon \epsilon_0}{e^2} \right]^{\frac{1}{2}} \left[\frac{e}{kT} (\Phi_0 - \Phi_{\infty}) - 1 \right]^{\frac{1}{2}} \text{ per meter}^2, \quad (2)$$

where $(\Phi_0 - \Phi_{\infty})$ is the voltage drop across the space charge layer, n_{∞}^- is the electron concentration in the crystal far from the surface, ϵ is the dielectric constant of ZnO which is 8.5,¹² and ϵ_0 is the permittivity of free space. A crystal with bulk conductivity of 0.01 (ohm cm^{-1}) has $n_{\infty}^- = 3.4 \times 10^{14}/\text{cc}$, for a bulk mobility of $180 \text{ cm}^2/\text{v sec}$. For a cylindrical crystal of radius r cm, a reasonable limiting value of the ratio

$$\frac{\text{Total number of charges on surface, } N_s}{\text{Total number of charges in bulk, } N_B} = \frac{2m^-}{rn_{\infty}^-} \quad (3)$$

and of m^- can be calculated since the voltage drop across the space-charge layer is not likely to be greater than about $20kT/e$ (0.5 volt at room temperature). Substituting this value into (2) gives a maximum value of $m^- = 4 \times 10^{10} \text{ cm}^{-2}$, and for Eq. (3) a maximum value of

$$\frac{N_s}{N_B} = \frac{2 \times 4 \times 10^{10}}{10^{-2} \times 3.4 \times 10^{14}} = 0.02.$$

An adsorbed oxygen layer could therefore affect the conductance by only 2%. Since for crystal 24L the conductance can be changed by a factor of 10, the destruction of a depletion layer contributes but little to the photoconductance.

The dark conductivity of crystal K-1 in vacuum indicates a value of n_{∞}^- near $1 \times 10^{14} \text{ cm}^{-3}$, corresponding to a reasonable maximum value of m^- of $2.2 \times 10^{10} \text{ cm}^{-2}$. It is interesting to notice in Fig. 6 that the quantum efficiency starts to decrease at about this value of surface conduction electron concentration, indicating that the quantum efficiency remains constant and quite high when the surface is negative, but decreases when the surface becomes positive. This conclusion is consistent with the fact that the lithium-doped crystals, which have a very low n_{∞}^- value, show no region of constant quantum efficiency since these crystals would have a concentration of adsorbed negatively charged oxygen ions less than 10^8 cm^{-2} .

The removal of a depletion layer could account for the effects if all the donors in the crystal were concen-

trated very close to the surface (see Heiland⁴), but etched crystals which show the full effects demonstrate that this explanation cannot be correct. Indeed the surface sensitivity of crystals doped with interstitial zinc on the one hand, and lithium on the other, shows that the effect is essentially independent of the donor concentration. It is unlikely that any adsorbed impurities could provide electrons for the enrichment layer and so the positive charges balancing the electrons must be associated with lattice atoms at the surface.

The model¹³ proposed is that the holes from hole-electron pairs produced by the light diffuse to the surface and are trapped on oxygen ions. Initially the adsorbed ions are neutralized and later the holes are trapped on surface lattice oxygen ions. As long as the adsorbed oxygen atoms are ionized, the surface of the crystal will be negative and will provide an attractive potential resulting in a high and constant quantum efficiency. After a sufficient number of positive holes have reached the surface to neutralize the adsorbed ions, e.g., when sample K-1 (Fig. 6) has about 2×10^{10} ions/cm², further diffusion will take place against a positive potential barrier. The height of the barrier increases with the number of trapped holes and eventually prevents the diffusion of holes to the surface. When an oxygen ion is discharged by the capture of a hole it may be thermally desorbed producing, in the case of the lattice oxygen ions, a surface excess of zinc atoms to act as donors. For decay to occur, it is now necessary that oxygen re-adsorption take place. It is perhaps surprising that even in one atmosphere of oxygen the re-adsorption is not very rapid, but the rate determining step may be the break-up of an oxygen molecule, requiring a considerable activation energy. Water may accelerate the rate either by acting as a catalyst or by reacting directly with the excess zinc.

The decomposition of a crystal by the action of light absorbed in the fundamental band is an example of photolysis and is well known for other materials. In the photographic process the photolysis of AgBr results in the formation of the latent image and the evolution of bromine with quantum efficiencies near unity.¹⁴ Since no space charge is formed in AgBr, the process proceeds indefinitely. Similarly the formation of visible quantities of metal by photolysis has been reported¹⁵ for CdS and ZnS.

At 78°K the results are very similar to those produced at room temperature and the same model should apply. However, the experiments showed that the extra conductivity produced by light decayed on warming near 170°K, suggesting that at 78°K the surface oxygen lattice ions which trap holes are not evolved as free gas atoms but remain on the surface. Near 170°K the re-

¹³ R. J. Collins and D. G. Thomas, Bull. Am. Phys. Soc. Ser. II, 2, 271 (1957).

¹⁴ G. W. Luckey, J. Chem. Phys. 23, 882 (1955).

¹⁵ W. J. Merz, Helv. Phys. Acta 30, 244 (1957).

¹² A. R. Hutson, Phys. Rev. 108, 222 (1957).

lease of the trapped holes or the capture of free electrons may begin to occur at an appreciable rate.

The supposition that excess zinc is produced at the surface is supported by the observations of Thomas and Lander⁶ on the conductivity of crystals with zinc adsorbed on their surfaces. Those curves in Fig. 4 which arose from illumination at room temperature are very similar in magnitude and shape to curves obtained by adsorbing different amounts of zinc onto ZnO crystals.

The surface lattice oxygen ions which trap holes may be regarded as donor surface states having a high density which lie in the forbidden gap above the top of the valence band. Since holes approaching the surface are destroyed by electrons from these donor states, it will be difficult to observe a *p*-type layer in a field-effect experiment.

It is unlikely that the value of 100 cm²/v sec assumed for the surface mobility is the precise value or that it

remains unchanged as the surface charge changes. Field-effect experiments now in progress,¹¹ are necessary to complete the interpretation of the present results. Nevertheless the mobility figure assumed cannot be in great error for the value cannot exceed the bulk value of 180 cm²/v sec, and if it were less than 20 cm²/v sec a quantum efficiency greater than unity would be observed for the initial portion of the photoconductive rise. From the magnitude of the quantum efficiency and the absorption coefficient measured by Mollwo,¹ one can see that the diffusion length of holes must be ≥ 500 Å.

ACKNOWLEDGMENTS

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Magnetic Anisotropy Constant of Yttrium Iron Garnet at 0°K*

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The anisotropy energy of yttrium iron garnet is separated into two parts, the normal part predominant at high temperatures, and the anomalous part important below 50°K. By comparison with ferrite data, the cause of the normal anisotropy is expected to be the coupling of the Fe³⁺ ions to the crystalline field. The following expression for K_1 , the first-order anisotropy constant, as a function of the fine structure coupling constants a_{24} (tetrahedral sites) and a_{16} (octahedral sites) is obtained: $K_1/\text{unit cell} = -46.6a_{24} - 13.6a_{16}$.

THE magnetocrystalline anisotropy of yttrium iron garnet (YIG) has unusual characteristics at low temperatures (below 50°K).^{1,2} Dillon gives a graph for K_1/M_s as a function of temperature. We have distinguished between two contributions to this curve: a normal part which predominates at high temperatures and an anomalous part which first appears at about 125°K. An attempt has been made to explain the normal contribution to K_1 by considering its value at 0°K. This value is -0.23 cm⁻¹ per unit cell (found by extrapolation from high-temperature data).

Several sources of the magnetic anisotropy energy have been discussed for antiferromagnetic and ferromagnetic substances.³⁻⁵ The relative importance of

these sources for YIG has been judged by comparison with the results obtained by Yosida and Tachiki for Mn- and Ni-ferrites.⁴ Just as for ferrites, the contribution of the classical dipolar interaction to the anisotropy vanishes identically because of the cubic symmetry of the crystal and spin lattice. The contribution from second-order dipole interaction is found to be only 10 to 15% of the experimental anisotropy energy for the ferrite case. The same is expected for YIG. For YIG, the contribution from anisotropic exchange interaction will be negligible because the orbital moment is zero in the ground state of Fe³⁺. The contribution from noncubic terms in the spin Hamiltonian, suggested by Wolf, is also negligible. It is therefore expected that the largest contribution to the anisotropy energy for YIG, as for ferrites, will come from the cubic crystalline field anisotropy. The author has estimated the anisotropy constant at $T=0$ from this source.

The Fe³⁺ ions are located at the centers of two types of coordination polyhedra of oxygen ions⁶; octahedra [16(a)] and tetrahedra [24(d)]. The anisotropy is caused by the interaction of the Fe³⁺ ions with the

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¹ J. F. Dillon, Jr., Phys. Rev. **105**, 759 (1957).

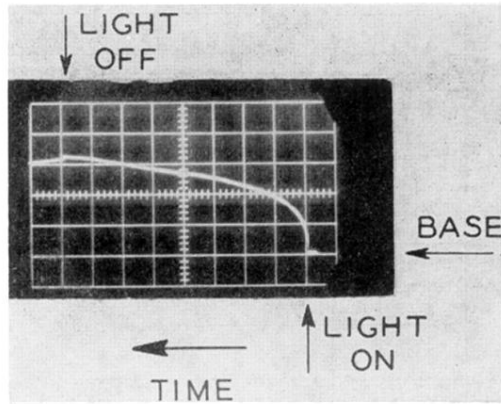
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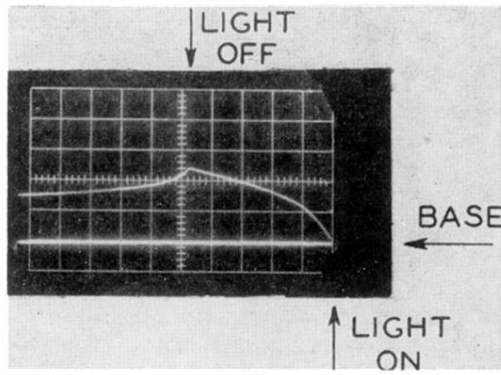
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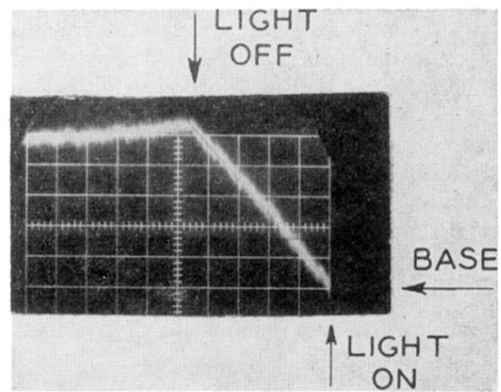
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(a)



(b)



(c)

FIG. 5. Room-temperature photoconductivity of crystal 24L in N_2 at 3131 Å. (a) 5.2×10^{14} photons/cm² sec. Vert., 500 mv/cm $\equiv 7.5 \times 10^{11}$ electrons/cm² cm. Horiz., 2 sec/cm. (b) 6.6×10^{12} photons/cm² sec. Vert., 10 mv/cm $\equiv 1.5 \times 10^{10}$ electrons/cm² cm. Horiz., 20 msec/cm. (c) 1.65×10^{11} photons/cm² sec. Vert., 0.1 mv/cm $\equiv 1.5 \times 10^8$ electrons/cm² cm. Horiz., 20 msec/cm.