Photoconductivity of Zinc Oxide under Different Ambient Conditions

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The existence of a close relationship between photoconduction and oxygen desorption process of zinc oxide has been made clear in some details since Bevan and Anderson's work[1]. The oxygen adsorbed on the surface of zinc oxide seems to produce an acceptor level for conduction electrons and to make a depletion layer under the surface. Destruction of the depletion layer or further formation of the space change layer[2] takes place accompanied by absorption of light, its wavelength is shorter than 4000 Å, and it yields a number of conduction electrons. This model well interprets the peculiarities of the photoconductive process of zinc oxide. Then, one can anticipate that the adsorption of other molecules than oxygen on a surface of zinc oxide too may give a similar or to some extent different effect on the dark- and photo-conduction of the material, depending upon the character of the adsorbant[3].

We have studied the effects of several kinds of ambient molecules on the surface conductivity of zinc oxide at room temperature. The

1) D. J. W. Bevan and J. S. Anderson, *Discussions Faraday Soc.*, No. 8, 238 (1950); D. B. Medved, *J. Chem. Phys.*, **28**, 870 (1958); D. A. Melnick, ibid., **26**, 1136 (1957); W. Ruppel, H. J. Gerritsen and A. Rose, *Helv. Phys. Acta*, **30**, 495 (1957).

2) R. J. Collins and D. G. Thomas, *Phys. Rev.*, **112**, 388 (1958).

3) V. I. Lyahenko and O. V. Snitko, *Trudy Inst. Fiz., Akad. Nauk, Ukr. USSR*, **91**, 1071 (1953); E. K. Putseiko and A. N. Terenin, *Doklady Akad. Nauk SSSR*, **101**, 645 (1955), *Problemy Kinetiki i Kataliza, Akad. Nauk SSSR*, **8**, 53 (1955).

specimens (ca. 20 μ in thickness) were made by depositing zinc oxide powder (Merck's reagent) from an ethanolic suspension on glass plates of 18×18 mm. in size. They possess parallel electrodes that are separated from each other by a gap of 5 mm. Silver paste was used as the electrode material. These specimens showed the values of $10^5 \sim 10^6$ times the initial conductivities measured in air ($10^{-11} \sim 10^{-13}$ ohm^{-1} for 20 V. of applied voltage) when they were kept in vacuum to remove the oxygen adsorbed on the zinc oxide layer. After this treatment, the gases or vapors were introduced onto the specimens and the dark currents were observed after 10 min.

The curves in Fig. 1 show the typical effect of an acceptor (O_2), a donor (NH_3) and a neutral (CO_2) type molecule on the dark

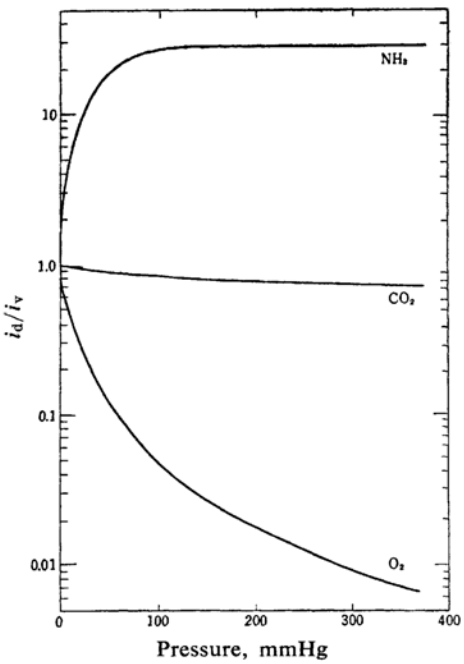

Fig. 1. Influence of the ambient gas on the dark conductivity of zinc oxide.
i_d: Dark current in the gas
i_v: Dark current in vacuum

conductivity. Ammonia was found to be effective on the electronic properties not only in vacuum but in atmospheric air. By pumping the ambient molecules off, the conductivity was unchanged in the case of oxygen, but in the case of ammonia, it returned to the initial value approximately. The behavior of nitrogen was quite similar to that of carbon dioxide and also methylamine to ammonia; otherwise the following three gases behaved as an acceptor type molecules; nitrogen oxide, nitrogen dioxide and methyl ethyl ketone (MEK). However, in the case of MEK, the conductivity was increased partly by taking it off. This seems to suggest that the nature of the adsorption was of somewhat different. Vapors of water, diethyl ether and ethyl alcohol did not change or slightly changed the conductivity of the zinc oxide cell.

As to the photoconductive sensitivity (i_p/i_d in Table I), a remarkable increase was found by adsorption of the electronegative gases such

TABLE I

Gas or vapor	Pressure mmHg	i_d/i_v	i_p/i_d	Decay
O_2	44	$\sim 10^{-2}$	$\sim 10^2$	rapid
NO	45	3×10^{-5}	$10^3 \sim 10^4$	rapid
NO_2	0.3	$<3\times10^{-5}$	$\sim 10^2$	very rapid
MEK	47	$10^{-2} \sim 10^{-3}$	2×10^2	slow
Vacuum	—	—	2～ 3	very slow
CO_2	114	1	2～ 3	very slow
NH_3	42	～10	2～ 3	slow
Pyridine	7.5	$10^{-2} \sim 10^{-4}$	—	—

i_v: Dark current in vacuum
i_d: Dark current in gas or vapor
i_p: Photocurrent in gas or vapor for 10^{12} photons/cm^2 sec. of 3650 Å light from an ultra-high pressure mercury lamp

as oxygen, nitrogen oxide and nitrogen dioxide, while no change was observed by adsorption of carbon dioxide or ammonia type molecules. In Table I, the results of qualitative observations on the rate of current decay after ceasing an irradiation on the cell were also tabulated. It is noteworthy that there exists a parallelism between the chemical activity of the ambient molecules and the rate of the decay process. The active electrons of these molecules may play an important role in the adsorption

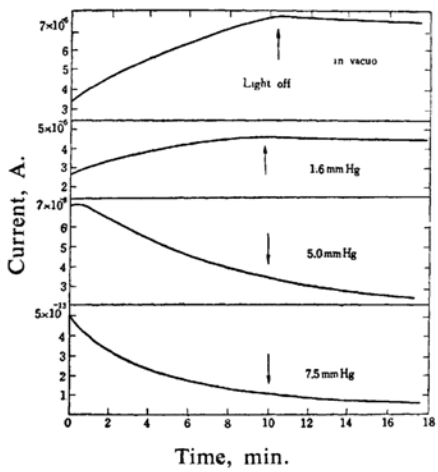

Fig. 2. Photoresponses of the conductivity of zinc oxide in pyridine vapor.

mechanism. MEK having no such active electrons, has only a weak effect to accelerate the decay[4].

The effect of aromatic and aliphatic hydrocarbons and also pyridine on the conductivity of zinc oxide were found to be rather obscure; the conductivity decreased by adsorption of these organic compounds. However, the irradiation on this system did not change the value of its conductivity; it monotonically decreased when an electric field was applied for measurement. This effect was more noticeable if the vapor pressure was increased, as shown in Fig. 2. The nature of this strange phenomenon is not yet clear.

4) By adsorbing ammonia or another donor type molecule too, a little higher decay rate is observed, associated with a greater density of recombination centers, with a greater capture cross section for the recombination, or with both (R. H. Bube, *Phys. Rev.*, **101**, 1668 (1956)).

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