

**UNCLASSIFIED**

---

---

**AD 404 651**

*Reproduced  
by the*

**DEFENSE DOCUMENTATION CENTER**

FOR

**SCIENTIFIC AND TECHNICAL INFORMATION**

**CAMERON STATION, ALEXANDRIA, VIRGINIA**



---

---

**UNCLASSIFIED**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

63-3-4

2900-400-R  
404651

CATALOGUED BY ASTIA  
AS AD NO.

Memorandum of Project MICHIGAN

# EFFECT OF CHEMISORBED OXYGEN ON PHOTOVOLTAIC AND PHOTOCONDUCTIVE PROCESSES IN RUTILE

R. KEEZER



INFRARED LABORATORY  
*Institute of Science and Technology*  
THE UNIVERSITY OF MICHIGAN

May 1963

Contract DA-36-039 SC-78801

DDC  
RECEIVED  
MAY 27 1963  
TISIA D

404651

2900 - 400 - R

Memorandum of Project MICHIGAN

**EFFECT OF CHEMISORBED OXYGEN ON  
PHOTOVOLTAIC AND PHOTOCONDUCTIVE  
PROCESSES IN RUTILE**

**R. KEEZER**

May 1963

Infrared Laboratory

*Institute of Science and Technology*

THE UNIVERSITY OF MICHIGAN

Ann Arbor, Michigan

## NOTICES

Sponsorship. The work reported herein was conducted by the Institute of Science and Technology for the U. S. Army Electronics Command under Project MICHIGAN, Contract DA-36-039 SC-78801. Contracts and grants to The University of Michigan for the support of sponsored research by the Institute of Science and Technology are administered through the Office of the Vice-President for Research.

Note. The views expressed herein are those of Project MICHIGAN and have not been approved by the Department of the Army.

Distribution. Initial distribution is indicated at the end of this document. Distribution control of Project MICHIGAN documents has been delegated by the U. S. Army Electronics Command to the office named below. Please address correspondence concerning distribution of reports to:

Commanding Officer  
U. S. Army Liaison Group  
Project MICHIGAN  
The University of Michigan  
P. O. Box 618  
Ann Arbor, Michigan

ASTIA Availability. Qualified requesters may obtain copies of this document from:

Armed Services Technical Information Agency  
Arlington Hall Station  
Arlington 12, Virginia

Final Disposition. After this document has served its purpose, it may be destroyed. Please do not return it to the Institute of Science and Technology.

## PREFACE

Project MICHIGAN is a continuing, long-range research and development program for advancing the Army's combat-surveillance and target-acquisition capabilities. The program is carried out by a full-time Institute of Science and Technology staff of specialists in the fields of physics, engineering, mathematics, and psychology, by members of the teaching faculty, by graduate students, and by other research groups and laboratories of The University of Michigan.

The emphasis of the Project is upon research in imaging radar, MTI radar, infrared, radio location, image processing, and special investigations. Particular attention is given to all-weather, long-range, high-resolution sensory and location techniques.

Project MICHIGAN was established by the U. S. Army Signal Corps at The University of Michigan in 1953 and has received continuing support from the U. S. Army. The Project constitutes a major portion of the diversified program of research conducted by the Institute of Science and Technology in order to make available to government and industry the resources of The University of Michigan and to broaden the educational opportunities for students in the scientific and engineering disciplines.

Documents issued in this series of Technical Memorandums are published by the Institute of Science and Technology in order to disseminate scientific and engineering information as speedily and as widely as possible. The work reported may be incomplete, but it is considered to be useful, interesting, or suggestive enough to warrant this early publication. Any conclusions are tentative, of course. Also included in this series are reports of work in progress which will later be combined with other materials to form a more comprehensive contribution in the field.

Progress and results described in reports are continually reassessed by Project MICHIGAN. Comments and suggestions from readers are invited.

Robert L. Hess  
Director  
Project MICHIGAN

**SYMBOLS**

t = time

k = conductance

Z = excitation rate

D = desorption rate of physically adsorbed atoms from surface to ambient pressures

b = a constant, dependent on the barrier layer formed by adsorbed atoms

p = the partial pressure of gas in equilibrium with the physically adsorbed atoms

C, A = constants

---

EFFECT OF CHEMISORBED OXYGEN ON PHOTOVOLTAIC AND  
PHOTOCONDUCTIVE PROCESSES IN RUTILE

ABSTRACT

It has been found that the presence of adsorbed oxygen increases both the response and the response time for the photovoltaic effect in rutile.

The model for the effect of chemisorbed oxygen on the photoconductivity has been modified to take into consideration the effect of oxygen pressure. The conductance of rutile has been measured as a function of oxygen pressure. The results agree with the modified model.

The increase in photovoltaic response and response time with exposure to oxygen has been explained in terms of the barrier layer formed by chemisorbed oxygen.

---

1

INTRODUCTION

During investigation of photovoltaic effects in rutile [ 1 ], it was noted that both the response time and the magnitude of response of a rutile photovoltaic device were affected by exposing the device to the atmosphere.

Figure 1 shows the configuration of the device. It was fabricated as follows. A polished single-crystal disk of rutile was reduced in a hydrogen environment at 600°C for two hours. The surface was then reoxidized by heating in air for ten minutes at approximately 600°C. A semitransparent silver electrode was evaporated onto one face, and a thick indium electrode was evaporated onto the opposite face.

2

EFFECT OF OXYGEN ON PHOTOVOLTAIC CHARACTERISTICS

The rise and decay of the photovoltage, as a result of pulsed ultraviolet radiation incident on the sample, was observed with an oscilloscope. Figure 2(a) shows the rise and decay characteristics of a sample which had been exposed to laboratory conditions for several days. Figure 2(b) illustrates the change in these characteristics as a result of pumping on the sample

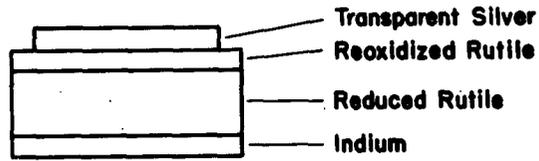


FIGURE 1. CONFIGURATION OF PHOTOVOLTAIC DEVICE

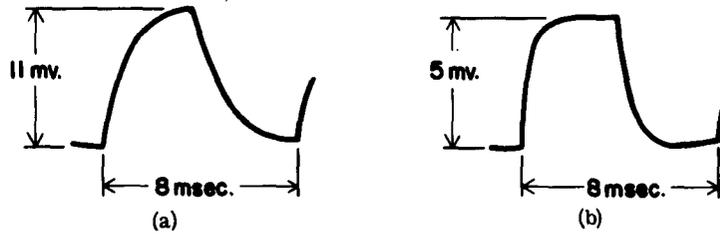


FIGURE 2. EFFECT OF OXYGEN ON PHOTOVOLTAIC CHARACTERISTICS.  
(a) In air. (b) In Vacuum.

continuously for five hours at  $10^{-4}$  mm Hg. The response time decreased from 1 msec to 1/2 msec, while the amplitude of the photosignal decreased by a factor of two. When the sample was exposed to air again, the response time and photosignal returned to their original values. This procedure was repeated several times with the same results; hence, the process appears to be reversible.

It was also observed that the rate at which the characteristics changed in vacuum depended to some extent on whether or not the sample was irradiated with ultraviolet light.

## 3

## PHOTOCONDUCTIVITY AND CHEMISORPTION

Miller [2] has discussed the effects of chemisorption on the performance of photoconductive devices. Melnick [3] and Morrison [4] have proposed a model for chemisorption on semiconductor surfaces during exposure to radiation. The model applies, in particular, to the interaction of oxygen with an n-type semiconductor such as rutile. They suggest that an oxygen atom is physically adsorbed on the surface of the semiconductor. There it combines with an electron from the valence band, thus becoming chemisorbed. Upon irradiation, holes and electrons are produced near the surface. The holes combine with a chemisorbed atom which is changed, at least transiently, to a physically adsorbed atom. The physically adsorbed atoms may then either combine with an electron or diffuse from the surface into the ambient gas. These phenomena cause a change in the free-carrier concentration, and hence a change in the conductance of the semiconductor.

The differential equation proposed by Melnick for the change of conductance on exposure to both oxygen and radiation is:

$$\frac{dk}{dt} = Z - D \exp(bk) + D \quad (1)$$

where  $t$  = time

$k$  = conductance

$Z$  = excitation rate

$D$  = desorption rate of physically adsorbed atoms from surface to ambient pressures

$b$  = a constant dependent on the barrier layer formed by adsorbed atoms

Equation 1 was used to derive the following equation for the photoconductive decay.

$$\Delta k = b^{-1} \ln (tbZ + 1) \quad (2)$$

Melnick [3], Medvid [5], and Elovich [6] have found that the photoconductive decay of zinc oxide follows Equation 2.

Another approach to this model is as follows. At equilibrium,  $dk/dt = 0$ . Therefore, at equilibrium, Equation 1 becomes

$$k = b^{-1} \ln[(Z + D)D^{-1}] \quad (3)$$

If one assumes the excitation rate  $Z$  to be large compared to the equilibrium desorption rate  $D$ , Equation 3 becomes

$$k = b^{-1} \ln ZD^{-1} \quad (4)$$

#### 4

#### RESULTS

In order to introduce the pressure as a variable, one may assume that the desorption rate is dependent on  $p$ , the partial pressure of gas in equilibrium with the physically adsorbed atoms. The Langmuir dependency

$$D = CAp/(1 + Ap) \quad (5)$$

may be used where  $C$  and  $A$  are constants. Combining Equations 4 and 5, one obtains

$$k = -b^{-1} \ln p + b^{-1} \ln[Z(1 + Ap)/AC] \quad (6)$$

For many systems  $A$  is of the order of  $10^{-4} \text{ mm}^{-1}$ . Therefore, at low pressures the second term in Equation 6 is a constant, and it may be constant up to several atmospheres.

A single crystal of rutile was cut and polished into a parallelepiped of dimensions  $1.6 \times 3.6 \times 15 \text{ mm}$ . Indium electrodes were evaporated onto the ends of the sample. The sample was placed in a dewar and irradiated continuously with ultraviolet light. The conductance at equilibrium was measured as a function of oxygen pressure. Figure 3 shows the results of these measurements. The conductance as a function of pressure follows Equation 6 over 5 orders of magnitude of pressure.

The proposed model predicts a slow change in conductance with pressure if the excitation rate is zero, since, without photo excitation, only thermally excited holes are available to

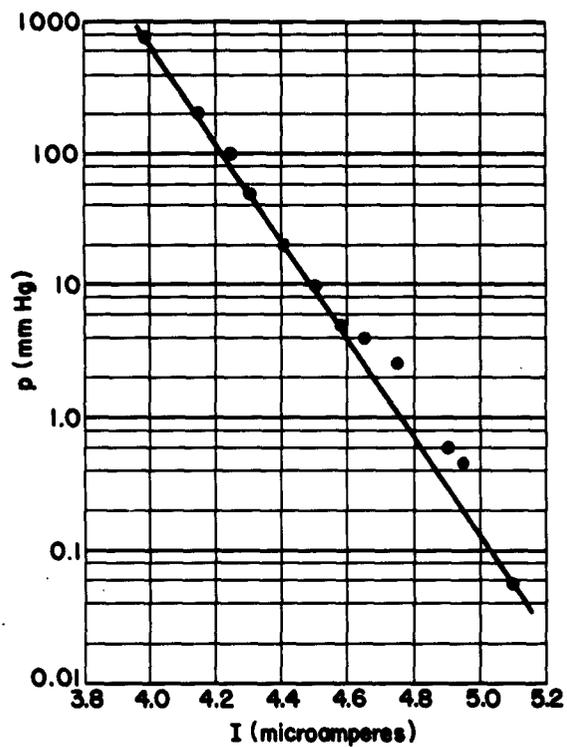


FIGURE 3. EFFECT OF OXYGEN ON PHOTOCONDUCTIVITY

convert the chemisorbed atoms to physically adsorbed atoms.

It was indeed found that if the sample was kept in the dark there was no change with pressure in the equilibrium conductance over the range of pressures and times used in these experiments.

## 5

## CONCLUSIONS

It appears that oxygen is chemisorbed on the surface of rutile. The observed increase in both the magnitude of the photovoltaic response and the response time in rutile (see Figure 2) may now be explained on the basis of the chemisorption of oxygen on rutile, as discussed above.

According to Hauffe and Pfeiffer [7], chemisorbed oxygen on the surface would produce a barrier layer of the Schottky-Mott type. This barrier should change the magnitude of the barrier formed by the silver-to-rutile contact. The increase in the photovoltaic signal indicates that this barrier is increased by the chemisorption of oxygen.

The chemisorbed oxygen layer would also increase the resistance of the device by reducing the electron concentration. Since it appears that the response time for these photovoltaic devices increases with increasing resistance [1], one would expect an increase in response time with increasing chemisorbed oxygen.

## REFERENCES

1. R. Keezer, J. Mudar, and D. E. Brown, Bull. Am. Phys. Soc., Ser. II, August 1962, Vol. 7.
2. P. H. Miller Jr., in R. G. Breckenridge ed., Photoconductivity Conference, John Wiley and Sons, New York City, N. Y., 1956, p. 287.
3. D. Melnick, Thesis, University of Pennsylvania, 1954.
4. S. P. Morrison, Thesis, University of Pennsylvania, 1952.
5. D. Medvid, Thesis, University of Pennsylvania, 1955.
6. S. Yu Elovich and J. Zhabrova, J. Phys. Chem. (U.S.S.R.), 1939, Vol. 13, p. 1761.
7. Hauffe and Pfeiffer, Z. Elektrochem., 1952, Vol. 56, p. 390.

**PROJECT MICHIGAN DISTRIBUTION LIST 5**  
**1 May 1963—Effective Date**

<u>Copy No.</u>	<u>Addressee</u>	<u>Copy No.</u>	<u>Addressee</u>
1	Commanding General U.S. Army Electronics Command Fort Monmouth, New Jersey ATTN: AMSEL-RD	51-52	Director, U. S. Naval Research Laboratory Washington 25, D. C. ATTN: Code 2027
2-3	Commanding General U. S. Army Electronics Command Fort Monmouth, New Jersey ATTN: AMSEL-CB	53	Commanding Officer U. S. Navy Ordnance Laboratory Corona, California ATTN: Library
4-33	Commanding Officer U. S. Army Electronics R & D Laboratory Fort Monmouth, New Jersey ATTN: SELRA/ADT	54	Commanding Officer & Director U. S. Navy Electronics Laboratory San Diego 51, California ATTN: Library
34	Commanding General U. S. Army Electronics Proving Ground Fort Huachuca, Arizona ATTN: Technical Library	55	Commander, U. S. Naval Ordnance Laboratory White Oak Silver Spring, Maryland ATTN: Technical Library
35-38	Director, U. S. Army Engineer Geodesy Intelligence & Mapping R & D Agency Fort Belvoir, Virginia (35) ATTN: Intelligence Division (36) ATTN: Research & Analysis Division (37) ATTN: Photogrammetry Division (38) ATTN: Strategic Systems Division (ENOGM-580)	56-60	ASTIA (TIPCA) Arlington Hall Station Arlington 12, Virginia
39	Director, U. S. Army Cold Regions Research & Engineering Laboratory P. O. Box 328 Hanover, New Hampshire	51-56	Commander Wright-Patterson AFB, Ohio (51-53) ATTN: ASD (ASRNOO) (54) ATTN: ASD (ASAPR-D) (55-56) ATTN: ASD (ASRNGE-1)
40-41	Director, U. S. Army Engineers Research & Development Laboratory Fort Belvoir, Virginia ATTN: Technical Documents Center	57-59	Commander, Rome Air Development Center Griffiss AFB, New York (57) ATTN: RAALD (58) ATTN: RAWIC (59) ATTN: RALBS
42	Commanding Officer U. S. Army Research Office (Durham) Box CM, Duke Station Durham, North Carolina ATTN: Chief Information Processing Office	90-94	Central Intelligence Agency 2430 E. Street, N. W. Washington 25, D. C. ATTN: OCR Mail Room
43	Assistant Commandant U. S. Army Air Defense School Fort Bliss, Texas	95-96	Scientific & Technical Information Facility P. O. Box 5700 Bethesda, Maryland ATTN: NASA Representative
44	Commandant U. S. Army Engineer School Fort Belvoir, Virginia ATTN: EBSY-L	97-98	National Aeronautics & Space Administration Manned Space Craft Center Houston 1, Texas ATTN: Chief, Technical Information Division
45	Commanding Officer U. S. Army Intelligence Combat Development Agency Fort Holabird Baltimore 19, Maryland	99	Cornell Aeronautical Laboratory, Incorporated Washington Projects Office Falls Church, Virginia ATTN: Technical Library
46	Commanding Officer, U. S. Army Electronic Research Unit P. O. Box 206 Mountain View, California ATTN: Electronic Defense Laboratories	100	The Rand Corporation 1700 Main Street Santa Monica, California ATTN: Library
47	U. S. Army Research Liaison Office MIT-Lincoln Laboratory Lexington 73, Massachusetts	101	Research Analysis Corporation 6935 Arlington Road Bethesda, Maryland Washington 14, D. C. ATTN: Chief, Information and Control Systems Division
48-49	Office of Naval Research Department of the Navy 17th & Constitution Avenue, N.W. Washington 25, D. C. (48) ATTN: Code 463 (49) ATTN: Code 461	102-103	Cornell Aeronautical Laboratory, Incorporated 4455 Genesee Street Buffalo 21, New York ATTN: Librarian VIA: Bureau of Naval Weapons Representative 4455 Genesee Street Buffalo 21, New York
50	The Hydrographer U. S. Navy Hydrographic Office Washington 25, D. C. ATTN: Code 1640		

## PROJECT MICHIGAN DISTRIBUTION LIST 5 (Continued)

<u>Copy No.</u>	<u>Addressee</u>	<u>Copy No.</u>	<u>Addressee</u>
104	Columbia University Electronics Research Laboratory 632 W. 12th Street New York 27, New York ATTN: Technical Library VIA: Commander, Rome Air Development Center Griffiss AFB, New York ATTN: RCKCS	107-109	Jet Propulsion Laboratory California Institute of Technology 4800 Oak Grove Drive Pasadena, California
105	Coordinated Science Laboratory University of Illinois Urbana, Illinois ATTN: Librarian VIA: ONR Resident Representative 805 S. Goodwin Avenue Urbana, Illinois	110	U.S. Naval Photographic Interpretation Center 4301 Bailland Road Washington 25, D. C.
106	The Ohio State University Research Foundation 1314 Kinnear Road Columbus 12, Ohio ATTN: Security Office VIA: Commander, Wright Air Development Division Wright-Patterson AFB, Ohio ATTN: ASRKBE	111	Commanding Officer, U. S. Army Liaison Group Project MICHIGAN The University of Michigan P. O. Box 618 Ann Arbor, Michigan

AD Div. 25/6

Inst. of Science and Technology, U. of Mich., Ann Arbor  
EFFECT OF CHEMISORBED OXYGEN ON PHOTVOL-  
TAIC AND PHOTCONDUCTIVE PROCESSES IN  
RUTILE, by R. Keezer. Memorandum of Project MICHIGAN. May 63. 6 p. incl. illus., 7 refs. (Memorandum No. 2900-400-R) (Contract DA-36-039 SC-78801) (Project No. 3D5801001) Unclassified Memorandum

It has been found that the presence of adsorbed oxygen increases both the response and the response time for the photovoltaic effect in rutile.

The model for the effect of chemisorbed oxygen on the photoconductivity has been modified to take into consideration the effect of oxygen pressure. The conductance of rutile has been measured as a function of oxygen pressure. The results agree with the modified model. (over)

Armed Services  
Technical Information Agency  
UNCLASSIFIED

UNCLASSIFIED

I. Title: Project MICHIGAN  
II. R. Keezer  
III. U. S. Army Electronics  
Command  
IV. Contract DA-36-039-78801  
V. Project No. 3D5801001

AD

Div. 25/6

Inst. of Science and Technology, U. of Mich., Ann Arbor  
EFFECT OF CHEMISORBED OXYGEN ON PHOTVOL-  
TAIC AND PHOTCONDUCTIVE PROCESSES IN  
RUTILE, by R. Keezer. Memorandum of Project MICHIGAN. May 63. 6 p. incl. illus., 7 refs. (Memorandum No. 2900-400-R) (Contract DA-36-039 SC-78801) (Project No. 3D5801001) Unclassified Memorandum

It has been found that the presence of adsorbed oxygen increases both the response and the response time for the photovoltaic effect in rutile.

The model for the effect of chemisorbed oxygen on the photoconductivity has been modified to take into consideration the effect of oxygen pressure. The conductance of rutile has been measured as a function of oxygen pressure. The results agree with the modified model. (over)

Armed Services  
Technical Information Agency  
UNCLASSIFIED

UNCLASSIFIED

I. Title: Project MICHIGAN  
II. R. Keezer  
III. U. S. Army Electronics  
Command  
IV. Contract DA-36-039-78801  
V. Project No. 3D5801001

AD

Div. 25/6

Inst. of Science and Technology, U. of Mich., Ann Arbor  
EFFECT OF CHEMISORBED OXYGEN ON PHOTVOL-  
TAIC AND PHOTCONDUCTIVE PROCESSES IN  
RUTILE, by R. Keezer. Memorandum of Project MICHIGAN. May 63. 6 p. incl. illus., 7 refs. (Memorandum No. 2900-400-R) (Contract DA-36-039 SC-78801) (Project No. 3D5801001) Unclassified Memorandum

It has been found that the presence of adsorbed oxygen increases both the response and the response time for the photovoltaic effect in rutile.

The model for the effect of chemisorbed oxygen on the photoconductivity has been modified to take into consideration the effect of oxygen pressure. The conductance of rutile has been measured as a function of oxygen pressure. The results agree with the modified model. (over)

Armed Services  
Technical Information Agency  
UNCLASSIFIED

UNCLASSIFIED

I. Title: Project MICHIGAN  
II. R. Keezer  
III. U. S. Army Electronics  
Command  
IV. Contract DA-36-039-78801  
V. Project No. 3D5801001

AD

Div. 25/6

Inst. of Science and Technology, U. of Mich., Ann Arbor  
EFFECT OF CHEMISORBED OXYGEN ON PHOTVOL-  
TAIC AND PHOTCONDUCTIVE PROCESSES IN  
RUTILE, by R. Keezer. Memorandum of Project MICHIGAN. May 63. 6 p. incl. illus., 7 refs. (Memorandum No. 2900-400-R) (Contract DA-36-039 SC-78801) (Project No. 3D5801001) Unclassified Memorandum

It has been found that the presence of adsorbed oxygen increases both the response and the response time for the photovoltaic effect in rutile.

The model for the effect of chemisorbed oxygen on the photoconductivity has been modified to take into consideration the effect of oxygen pressure. The conductance of rutile has been measured as a function of oxygen pressure. The results agree with the modified model. (over)

Armed Services  
Technical Information Agency  
UNCLASSIFIED

UNCLASSIFIED

I. Title: Project MICHIGAN  
II. R. Keezer  
III. U. S. Army Electronics  
Command  
IV. Contract DA-36-039-78801  
V. Project No. 3D5801001

UNCLASSIFIED  
DESCRIPTORS  
Surface properties  
Adsorption  
Photoconductivity

AD  
The increase in photovoltaic response and response time with exposure to oxygen has been explained in terms of the barrier layer formed by chemisorbed oxygen.  
(Unclassified abstract)

UNCLASSIFIED  
DESCRIPTORS  
Surface properties  
Adsorption  
Photoconductivity

AD  
The increase in photovoltaic response and response time with exposure to oxygen has been explained in terms of the barrier layer formed by chemisorbed oxygen.  
(Unclassified abstract)

UNCLASSIFIED

+

UNCLASSIFIED

UNCLASSIFIED  
DESCRIPTORS  
Surface properties  
Adsorption  
Photoconductivity

AD  
The increase in photovoltaic response and response time with exposure to oxygen has been explained in terms of the barrier layer formed by chemisorbed oxygen.  
(Unclassified abstract)

UNCLASSIFIED  
DESCRIPTORS  
Surface properties  
Adsorption  
Photoconductivity

AD  
The increase in photovoltaic response and response time with exposure to oxygen has been explained in terms of the barrier layer formed by chemisorbed oxygen.  
(Unclassified abstract)

UNCLASSIFIED

UNCLASSIFIED