Effect of Chemisorbed Oxygen on Photovoltaic and Photoconductive Processes in Rutile*

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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, measured as a function of oxygen pressure, agrees 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.

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 2 h. The surface was then reoxidized by heating in air for 10 min at approximately 600°C. A semitransparent silver electrode was deposited from the vapor onto one face, and a thick indium electrode was deposited onto the opposite face.

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 continuously for 5 h at 10^{-4} Torr. The response time decreased from 1 to $\frac{1}{2}$ 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.

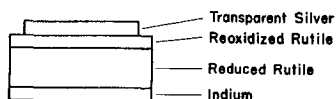It was also observed that the rate at which the

characteristics changed in vacuum depended to some extent on whether the sample was irradiated with ultraviolet light.

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 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:

$$dk/dt = Z - D \exp(bk) + D, \qquad (1)$$

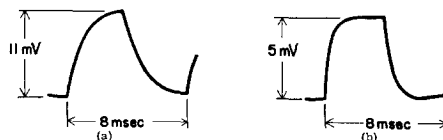where t = time, k = conductance, Z = excitation rate, D = desorption rate of physically adsorbed atoms from

Fig. 1. Configuration of photovoltaic device.

Transparent Silver
Reoxidized Rutile
Reduced Rutile
Indium

[1] R. Keezer, J. Mudar, and D. E. Brown, Bull. Am. Phys. Soc. 7, 495 (1962).

Fig. 2. Effect of oxygen on photovoltaic characteristics: (a) in air; (b) in vacuum.

[2] P. H. Miller, Jr., *Photoconductivity Conference*, edited by R. G. Breckenridge (John Wiley & Sons, Inc., New York, 1956), p. 287.
[3] D. Melnick, thesis, University of Pennsylvania (1954).
[4] S. R. Morrison, thesis, University of Pennsylvania (1952).

the surface, and $b=$ a constant dependent on the barrier layer formed by adsorbed atoms.

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

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

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

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

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

If one assumes the excitation rate Z to be large compared to the equilibrium desorption rate D, Eq. (3) becomes

$$k = b^{-1} \ln ZD^{-1}. \tag{4}$$

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

$$D = CAp/(1+Ap) \tag{5}$$

may be used where C and A are constants. Combining Eqs. (4) and (5), one obtains

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

For many systems A is of the order of 10^{-4} mm^{-1}. Therefore, at low pressures the second term in Eq. (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 $1.6 \times 3.6 \times 15$ mm. Indium electrodes were deposited onto the small faces of the sample. The sample was placed in a Dewar and irradiated continuously with 3650-Å ultraviolet light. The light intensity was about 10^{-2} W/cm^2. High purity oxygen was dried at liquid-nitrogen temperature. The dry oxygen was then allowed to warm to room temperature before being admitted to the sample Dewar. 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 Eq. (6) over 5 orders of magnitude of pressure.
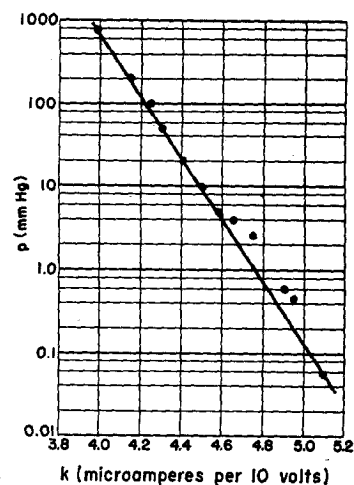
The proposed model predicts a slow change in con-

⁵ D. Medvid, thesis, University of Pennsylvania (1955).
⁶ S. Yu Elovich and J. Zhabrova, J. Phys. Chem. (USSR) **13**, 1761, 1775 (1939).

Fig. 3. Effect of oxygen on photoconductivity.

k (microamperes per 10 volts)

ductance with pressure if the excitation rate is zero, since, without photoexcitation, only thermally excited holes are available to 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.

Since only two terminal measurements were made, it is not known to what extent the chemisorbed oxygen affects the contact resistance of the indium to rutile electrode.

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 Fig. 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, one would expect an increase in response time with increasing chemisorbed oxygen.

⁷ K. Hauffe and H. Pfeiffer, Z. Elektrochem. **56**, 390 (1952).