

## Photovoltaic Effects in Rutile\*

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The ultraviolet photovoltaic response of barrier-layer cells formed from single-crystal rutile has been investigated. Typical samples have response maxima at 3200 Å, a  $D^*$  of  $10^9$  cm cps<sup>1/2</sup>/W, and time constants of 100 μsec. Variations in time constant over several orders of magnitude have been observed, dependent largely on preparative technique. The effect of surface treatment on cell characteristics is discussed.

### INTRODUCTION

VARIOUS workers have shown that when rutile, an oxide of titanium, is heated in a reducing environment, the resistivity decreases from that of an insulator to several Ω-cm.<sup>1,2</sup> The resulting resistivity depends on the degree of reduction. The process is reversible; that is, a reduced, low-resistivity sample can be restored to its original high resistivity by heating in an oxidizing atmosphere.

There is considerable discussion at present whether the excess conductivity associated with the reduced condition is associated with oxygen vacancies or with interstitial titanium ions.<sup>3</sup>

Photoconductivity in rutile has been reported by Cronmeyer,<sup>4</sup> and by Townsend, Kan, and Levy.<sup>5</sup> Optical measurements by various workers indicate an intrinsic energy gap of between 3 and 4 eV.<sup>4,5</sup>

Breckenridge and Hosler<sup>6</sup> have observed rectification effects at contacts between oxidized titanium and various other metals (with indium used as an Ohmic contact).

We have observed a photovoltaic effect at barrier layers between rutile and silver.<sup>7</sup>

### EXPERIMENTAL STUDY

A single-crystal boule of rutile was obtained from the Linde Company. Disks about 13 mm in diameter and 1 mm thick were cut from the boule, and the faces were ground and polished. Electrodes were deposited from the vapor onto the flat surfaces—indium on one surface, and semitransparent silver on the other.

Exposing the silver electrode to ultraviolet radiation generated a photovoltage across the sample; pulses in the radiation caused the photovoltage to rise and decay.

These variations were observed on an oscilloscope, and the time constant of each sample was obtained from the slope of the plot of ln (decay of response) vs time. As Fig. 1 shows, these samples had multiple time constants.

Other samples, with shorter time constants, were prepared by partially reducing the rutile in a hydrogen environment at 600°C. The response time of these samples varied from 3 to 20 msec. Multiple time constants were not observed.

Samples with time constants of 100 μsec and less were prepared as follows. The rutile disks were reduced for several hours in a hydrogen atmosphere at 600°C. The samples were slowly cooled in a hydrogen environment. The surface was then reoxidized by heating the samples in air. As Table 1 shows, the time constants of the

TABLE I. Effect of reoxidation on time constant of photovoltaic response of rutile detectors.

Sample	Reduction time at 600°C, h	Oxidation time, min	Oxidation temperature	dc resistance, Ω		Time constant, msec
				Reverse bias	Forward bias	
1-F	2	10	625°C	2600	1500	15
2-F	2	10	600°C	560	555	0.25
3-F	2	10	550°C	140	140	0.1
4-F	2	10	500°C	120	120	0.1

samples increased from 100 μsec to 15 msec as the amount of reoxidation increased.

The magnitude of the photovoltaic response and time constant were reduced when the ambient pressure was reduced to 10<sup>-4</sup> Torr.<sup>8</sup>

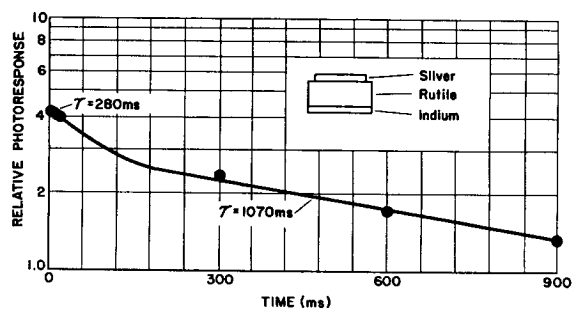


FIG. 1. Multitime constant detector.

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<sup>8</sup> R. C. Keezer, J. Appl. Phys. **35**, 1866 (1964) (this issue).

Relative spectral response measurements indicated peaks at 3200 Å. (Cronmeyer<sup>4</sup> has reported that the peak relative response for the photoconductive effect is at 4000 Å.) Figure 2 shows the spectral response characteristics of several samples. The best samples have  $D^* = 5 \times 10^9$  cm cps<sup>1/2</sup>/W at 3200 Å.<sup>9</sup> The external transmission of the semitransparent silver electrode, also shown in Fig. 2, was obtained by placing a sapphire disk adjacent to the samples during the deposition of the silver.

The experimental apparatus used to obtain the spectral characteristics of these samples is shown in Fig. 3.

In order to determine the mechanism of these reduced reoxidized samples, a series of detectors were prepared under various conditions.

First, four rutile samples were reduced at the same temperature for the same length of time. Two samples were reoxidized. Indium and silver electrodes were vapor deposited on all four samples. The two samples which had not been reoxidized were not photovoltaic, whereas the reoxidized samples were. This indicated that the oxidized layer was necessary and that "fully" reduced samples were not photovoltaic.

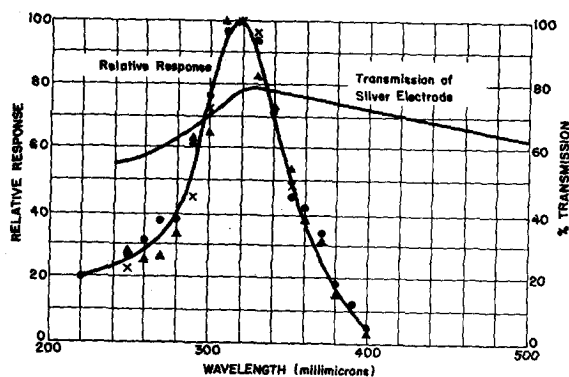


FIG. 2. Spectral characteristics of detectors and electrode.

<sup>9</sup>  $D^* = (\text{bandwidth}/A)^{1/2} (\text{signal}/\text{noise}) (\text{flux density})^{-1}$ .

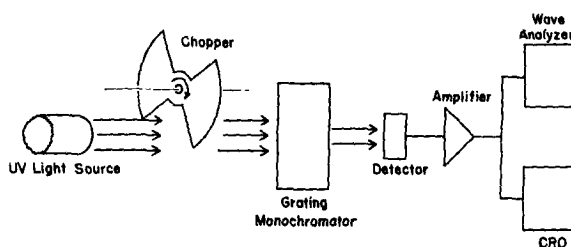


FIG. 3. Spectral-response measuring equipment.

Four more samples were reduced and reoxidized together. Indium was deposited on the back of all four samples, and a semitransparent layer of indium on the front of two samples. A semitransparent silver layer was deposited on the front of the other two. The samples with silver as the front electrode were photovoltaic, but the samples with the indium as the front electrodes were not. This indicated the barrier layer is formed between the silver and the reoxidized rutile, and not between the reduced rutile and the reoxidized rutile.

## CONCLUSIONS

We propose the following model for the mechanism of the reduced reoxidized rutile photovoltaic detector. First, the sensitive region or barrier layer occurs at the junction between the silver and the reoxidized rutile. Photons are absorbed near this junction and create hole-electron pairs. The holes and electrons which diffuse to the barrier layer cause a photovoltaic effect. Peak response occurs at that wavelength for which the absorption coefficient is high enough that the excess carriers are generated within a diffusion length of the barrier layer, but not so high that surface recombination effects reduce the responsivity. Increasing reoxidation causes an increase in the effective time constant by increasing the resistance of inactive bulk  $\text{TiO}_2$  in series with the active barrier layer.

The bulk of the sample, which remains strongly reduced, acts as an Ohmic contact to the reoxidized rutile layer.