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Report of Project MICHIGAN

PHOTOCONDUCTIVITY IN SINGLE-CRYSTAL TELLURIUM

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Robert L. Hess
Technical Director
Project MICHIGAN

FIGURES

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PHOTOCONDUCTIVITY IN SINGLE-CRYSTAL TELLURIUM

ABSTRACT

Measurements are reported of the photoconductive properties of tellurium crystals grown from the vapor phase as well as from the melt. The results are compared with measurements of other types of photoconductive cells and with theoretical estimates of the cell detectivity. For the "best" tellurium cell the measured detectivity at the spectral peak was $D^*_\lambda(3.4\ \mu,\ 900) = 2.3 \times 10^{11}$ cm-cps$^{1/2}$/watt compared with the estimated value of $D^*_\lambda(3.4\ \mu) = 2.2 \times 10^{11}$ cm-cps$^{1/2}$/watt. This is evidence that the tellurium photoconductive cell may be constructed to be background-radiation limited.

Tellurium single crystals grown from either the vapor phase or the melt produce photoconductive effects comparable to lead sulfide photoconductive cells. In the present paper, measurements are reported for several tellurium photoconductive cells and the results compared with other types of photoconductive cells and with theoretical estimates of the cell characteristics.

The use of tellurium as a photoconductive element was first investigated by Moss (see References 1 and 2), who used evaporated thin films. For a cell cooled to liquid nitrogen temperature, he reported a detectivity[1] value of $D^*_\lambda(1\ \mu,\ 80) = 1.7 \times 10^9$ cm-cps$^{1/2}$/watt, and a response time of about 550 μsec for the cell having the greatest detectivity. This same tellurium film had only a moderate detectivity $\left[D^*_\lambda(1\ \mu,\ 80) = 10^5 \text{ to } 10^6 \text{ cm-cps}^{1/2}/\text{watt}\right]$ at room temperature. Loferski (see Reference 3) later made photoconductivity measurements

[1]The conditions of measurement of the detectivity are specified in the expression $D^*_\lambda(1\ \mu,$ 80 cps) where the * indicates that the cell area and amplifier bandwidth have been normalized to 1 cm^2 and 1 cps, respectively; the subscript λ indicates that the monochromatic detectivity is for the wavelength specified by the first number in parenthesis. The second number in the parenthesis is the chopping frequency of the radiation. For the case in which a 500^{o}K blackbody is used as the radiation source, the λ subscript is omitted and the 1 μ is replaced by 500^{o}K, e.g., D*(500^{o}K, 80 cps).

on cooled single crystals of tellurium with about the same results as Moss had found for the cooled evaporated films. The single crystals used by Loferski were cleaved from large tellurium crystals and etched to the desired dimensions. Nickel was electroplated to the ends of the samples before soldering the copper leads. The impurity concentration of these crystals was estimated by Loferski to be about 10^{15} cm^{-3}.

Suits (see Reference 4) in 1957 found that thin hexagonal crystal prisms of tellurium when cooled to liquid nitrogen temperature had detectivities and response times comparable to those of cooled PbS cells. These thin single-crystal prisms (about 10 mm x 1/2 mm x 1/2 mm) were grown from the vapor phase in a low-pressure hydrogen atmosphere starting with 99.999+ percent pure material,[2] and always resulted in a needle-like cell element. The electrical contacts were made by welding a wire, in most cases platinum, to the tellurium. The crystal was then mounted in a glass dewar with a sapphire window similar to the dewar shown in Figure 1. Tellurium cells[3] having large detectivities have also been made from samples cleaved from melt-grown tellurium single crystals. Cells with sensitive elements as large as 16 mm^2 have been made in this way. The single crystals grown by the Czochralski methods along the C-axis (see Reference 6), were found to have low etch pit counts (as low as 1000 cm^{-2}) and long carrier lifetime (~70 μsec at 300°K), indicating a high degree of perfection (see Reference 7). Blakemore et al., report a change in room-temperature lifetime from 70 μsec to about 1 μsec for an increase in the defect density from 10^4 cm^{-2} to 10^6 cm^{-2}. Thus, the carrier lifetime is sensitively dependent on the defect density. The highest lifetime value previously reported (see Reference 8) was 0.01 μsec, probably indicating a large defect density (about 10^8 to 10^9 cm^{-2}).

Since tellurium can be plastically deformed under relatively small stresses, caution must be taken in preparing the tellurium samples to preserve the high degree of perfection. This is true for the vapor-phase-grown crystals (Te-N) as well as the melt-grown ones (Te-C).[4]

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[2] Obtained from American Smelting and Refining Company, South Plainfield, New Jersey.

[3] A preliminary report of tellurium cells utilizing large single crystals was presented in Reference 5.

[4] As a convenience in referring to these two types of tellurium cells, the cells made with vapor-phase-grown elements will be given the suffix N (e.g., Te-N or Te-59-N), meaning needle-like, and the suffix C (e.g., Te-C or Te-100-C) for cells with elements cleaved from large single crystals.

For the elements used in the Te-C cells, the electrical contacts were made of evaporated gold to which the leads were soldered. This method was adopted for these elements of larger area to reduce the effects of current-density variation across the element. The gold contacts also helped to define the sensitive area. Figure 2 is an end-on view of a mounted tellurium element cleaved from a melt-grown crystal, with evaporated gold electrodes. The sensitive area is about 2 mm x 2 mm.

The electrical noise, 500°K blackbody detectivity, and spectral detectivity were measured for a number of tellurium cells. For making these measurements the Te-N cells were connected directly across the primary of a G-5 Geoformer[5] whose impedance was approximately matched to the cell dark resistance. For the Te-C cells, a low-noise transistor preamplifier was used. At optimum bias, the noise of the Te-C cells was considerably greater than the preamplifier noise. Typical noise voltage values in a 5-cycle bandwidth vs. frequency curves for both types of cells are shown in Figure 3. For cell Te-59-N, the noise voltage is given for the optimum bias and zero bias. For this latter case, the noise voltage is approximately frequency independent and equal to the thermal noise of the cell (2 mμv for 200 Ω at 77°K and 5-cycle bandwidth). For optimum bias, i.e., the applied bias that produces maximum signal-to-noise ratio, the noise voltage for Te-59-N and Te-100-C are both typical semiconductor noise, i.e., the noise power has a 1/f frequency dependence. The increased noise at 10 kcs for cell Te-59-N with and without bias is produced by the increased transformer losses at high frequencies.

The spectral detectivity, D^*_λ, is shown in Figure 4 for a typical Te-N and Te-C cell. Also shown for comparison are curves for a few typical cells of different materials having D^*_λ curves competitive with those of the Te cells. Two curves are shown for the lead sulfide cells, PbS-I and PbS-II, to illustrate the two variations possible for this material. The PbS-I is the standard Eastman Type-N cell and PbS-II is the Eastman plumbide variation called Type-P. For PbS cells of the type represented by curve PbS-I, D^*_λ at the spectral peak is greater at 198°K than at 77°K, and has a long-wavelength cutoff of about 3.5 μ at 77°K. For cells of the type PbS-II, D^*_λ is greater at 77°K than at 198°K, and has a long-wavelength cutoff of about 4.5 μ at 77°K, and in general D^*_λ at the spectral peak is greater for the PbS-I type cells than for the PbS-II cells. The temperature effect for the two types of PbS cells has also been observed by Spencer (see Reference 9) who attributes the effect to the rate of absorption of ambient photons at the two temperatures.

[5] Made by Triad Transformer Corporation, Venice, California.

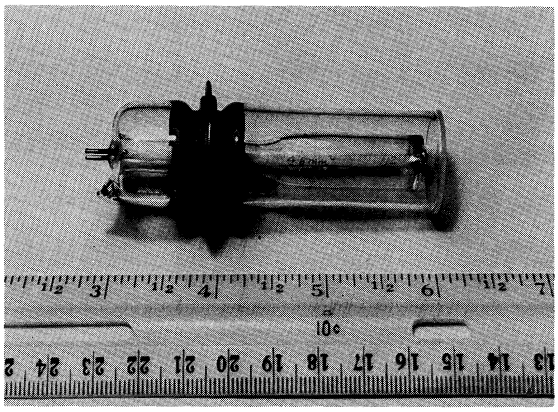

FIGURE 1. GLASS DEWAR WITH SAPPHIRE WINDOW

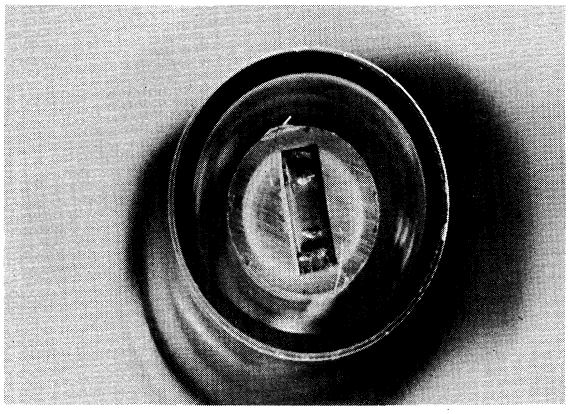

FIGURE 2. MOUNTED TELLURIUM ELEMENT CLEAVED FROM MELT-GROWN CRYSTAL

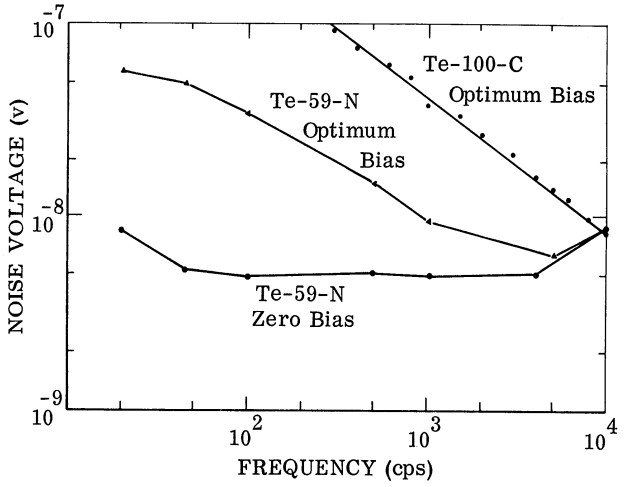

FIGURE 3. NOISE VOLTAGE SPECTRA FOR TWO TYPES OF TELLURIUM CELLS

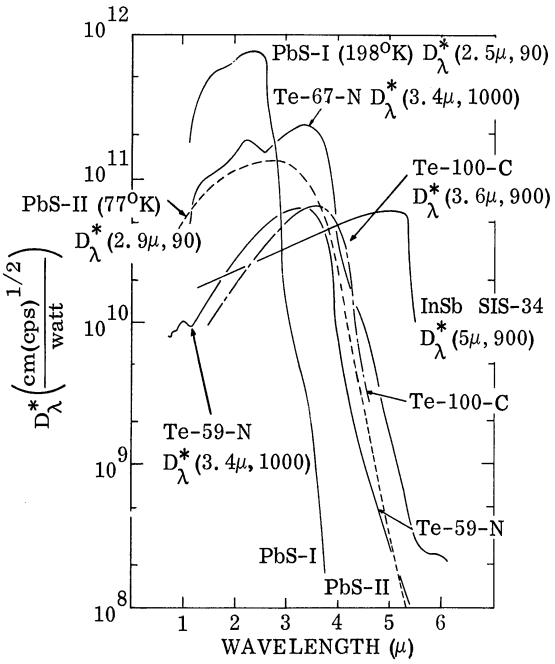

FIGURE 4. SPECTRAL DETECTIVITY FOR TELLURIUM, INDIUM ANTIMONIDE, AND LEAD SULFIDE PHOTOCONDUCTIVE CELLS

At low temperatures the noise of the cell is determined by the fluctuations in the carrier concentration produced by the background divided by the associated time constant (i.e., fluctuations in the rate of absorption). The photoabsorption for both types of PbS cells is greater at 77°K than at 198°K, and the time constant in the range from 77°K to 198°K remains about the same for the type I cells but becomes considerably shorter for the type II cells. Thus, the rate of absorption (and also the noise) for the type I cells is greater at 77°K than at 198°K whereas just the opposite is true for the type II cells. Since D^* is inversely proportional to the rate of absorption, then for the type I cells $D^*_{198^\circ} > D^*_{77^\circ K}$ and for type II cells $D^*_{77^\circ K} > D^*_{198^\circ K}$. The difference in the long-wavelength cutoffs for type I and II cells is also explained by Spencer as due to the temperature dependence of the rate of absorption.

The curve for the InSb cell shown in Figure 4 is for a photoconductive cell reported by Bratt et al. (see Reference 10). The cell temperature was 77°K, and a cooled aperture was used to restrict the field of view to a 60° cone. The effect of the cooled aperture is to increase D^*_λ by about 1.5 times. Roberts (see Reference 11) has reported D^*_λ values as great as 10^{11} cm-cps$^{1/2}$/watt at $\lambda = 5.3\ \mu$ for InSb photoconductive cells of similar design.

From Figure 4 it can be seen that cells Te-59-N and Te-100-C have very similar D^*_λ curves. The difference in the spectral peaks for these two cells is a surface effect as pointed out by Loferski (see Reference 3). The long-wavelength edge for Te-100-C and Te-59-N is almost identical with that of cell PbS-II. At $\lambda = 3.4\ \mu$ the D^*_λ value for PbS-II is about 1.5 times that of the Te cells and increases for shorter wavelengths. The time constant for the Te cells is about 60-120 μsec compared with about 4000 μsec for the PbS-II cell. Thus, for applications where the shorter time constant is required and the increased D^*_λ for $\lambda < 3\ \mu$ is unimportant, the Te cells should be superior to the PbS-II cell. Except for a narrow spectral region centered about 3.6 μ, the D^*_λ values are greater for the InSb cell than for the Te cells. The time constant for these InSb cells is of the order of 1 μsec. Thus the InSb cell appears to be superior to the Te cells in applications where rapid response times are important. By placing an optical filter having the long wavelength response of the Te cells in front of an InSb cell, one would have the advantages of the short time constant of the InSb cell and the spectral detectivity of the Te cell with little loss in D^*_λ at $\lambda = 3.6\ \mu$.

Also shown in Figure 4 is the D^*_λ curve for the tellurium cell, labeled Te-67-N, having the greatest detectivity measured so far. At the spectral peak, 3.4 μ, the D^*_λ for Te-67-N is about 4 times that for Te-59-N and Te-100-C. The noise spectrum for cell Te-67-N is very similar to that for cell Te-59-N (Figure 3). Without an applied bias, the noise is approximately frequency independent and about equal to the thermal noise of the cell (1 mμv for 96 Ω at 77°K

and 5-cycle bandwidth). With an applied bias, the noise power is 1/f semiconductor noise. The performance characteristics are given in Table I for the three tellurium cells, Te-100-C, Te-59-N, and Te-67-N.

TABLE I. CHARACTERISTICS OF TELLURIUM SINGLE-CRYSTAL PHOTOCONDUCTIVE CELLS AT 77°K

	Te-100-C	Te-59-N	Te-67-N
$D^*(500^oK, 90)\left(\frac{cm\text{-}cps^{1/2}}{watt}\right)$	1.3×10^9	1.3×10^9	6.2×10^9
$D^*(500^oK, 900)\left(\frac{cm\text{-}cps^{1/2}}{watt}\right)$	4×10^9	4.7×10^9	1.7×10^{10}
$D^*_\lambda(\lambda, 90)\left(\frac{cm\text{-}cps^{1/2}}{watt}\right)$	2×10^{10}	1.7×10^{10}	8.3×10^{10}
$D^*_\lambda(\lambda, 900)\left(\frac{cm\text{-}cps^{1/2}}{watt}\right)$	6.4×10^{10}	6.2×10^{10}	2.3×10^{11}
λ (spectral peak) (μ)	3.6	3.4	3.4
τ (time constant) (μsec)	~60	~120	~120
R (resistance) (Ω)	1000	199	96
A (area) (cm^2)	0.02 x 0.02	0.05 x 0.05	0.05 x 0.05

Recently, several articles have been published (see References 12-14) that describe methods for calculating the ultimate detectivity of a cell assuming that the limitations are fluctuations of the background radiation. Petritz (see Reference 12) has simplified the problem to a relation between the intrinsic energy gap, E_i, and the spectral detectivity, D^*_λ. Taking the optical activation energy to be 0.37 ev as given by Moss (see Reference 1), the ultimate detectivity would be $D^*_\lambda = 6 \times 10^{11}$ cm-cps $^{1/2}$/watt, about 2.5 times greater than the measured value for Te-67-N. One disadvantage of this method of estimating D^*_λ is that a knowledge of the intrinsic energy gap is required. In most cases, the value of the energy gap has been assigned somewhat arbitrarily. Moss takes the energy gap to be defined by the condition that the photocurrent is 50 percent of the peak photocurrent. Loferski (see Reference 3) takes the energy gap to be defined by the condition that the transmission is 5 percent of its value in the transparent region, i.e., $E_i = 0.325$ ev. This corresponds to a $D^*_\lambda = 3 \times 10^{11}$ cm-cps$^{1/2}$/watt. Another definition sometimes used is that the value of the energy gap corresponds to an absorption

coefficient 10^3 times the value in the transmission region. For this energy gap (E_i = 0.275 ev), $D^*_\lambda = 1.6 \times 10^{11}$ cm-cps$^{1/2}$/watt. Other authors have used still different definitions for the energy gap. For the case of tellurium, the definition of the energy gap is further complicated by the fact that the crystal is dichroic. These difficulties can be bypassed to some extent by calculating the ultimate detectivity after the method of Moss (see Reference 13). Here a knowledge of the intrinsic energy gap is not necessary. By this method, the ultimate detectivity is estimated (see Reference 15) to be D^*_λ (3.4 μ, -) = 2.2×10^{11} cm-cps$^{1/2}$/watt, compared with the measured value of D^*_λ (3.4 μ, 1000) = 2.3×10^{11} cm-cps$^{1/2}$/watt. This excellent agreement between the measured and estimated D^*_λ values is somewhat fortuitous because of the simplifying approximations made in this method of calculation.

It can be seen from both methods for estimating the theoretical D^*_λ value that the detectivity of cell Te-67-N is limited by the fluctuations of the background radiation. A possible explanation as to why the D^*_λ values of the other Te cells are less than that for Te-67-N is in the relative number of defects in the sensitive cell elements. From the study of whisker growth, it is known that the number of defects increases with the crystal diameter. One might then conclude that the Te-C elements cleaved from large crystals would intrinsically have a greater number of defects than the Te-N elements. Also, as pointed out earlier, tellurium can be easily deformed plastically, thereby introducing a large number of defects. The number of defects are intimately related to the time constant and thus to the detectivity (see Reference 9). Unfortunately, it was not possible to obtain estimates of the defect densities for any of the Te cell elements measured after they had been assembled. Investigations along this line are being continued.

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