Photoconductivity in Single-Crystal Tellurium*†

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Measurements of the steady-state and transient photoconductive behavior in the extrinsic range are presented and interpreted in terms of a simple trapping model. The change of electrical conductivity due to steady irradiation by light of 3.5-μ wavelength is proportional to the first power of the intensity of the light for low excitation, becoming proportional to the square root at higher excitation. The small signal responsive time constant is 350 μsec for $T<77°$K in the dark and decreases with either thermal or optical excitation. A model composed of 0.5×10^{13} traps/cm^3 of energy level 0.072 eV above the top of the valence band and an unspecified recombination mechanism account quantitatively for the observed effects. Details of the sample preparation process are given.

I. INTRODUCTION

THE element tellurium was discovered by von Reichenstein in 1782 and found to be a photoconductor by Bartlett[1] in 1925. However, only since 1957 have large single crystals been available[2] which are sufficiently perfect to permit detailed investigation of their photoconductive properties. The present study was undertaken to measure the steady-state and transient photoconductive behavior of single-crystal tellurium and to interpret the results in terms of a trapping model. We are concerned here only with the average values; the random fluctuations of electrical conductivity will be discussed elsewhere.[3]

The first physical studies of tellurium were directed toward its mechanical and electrical properties. In 1938 Bridgeman[4] measured electrical resistivity as a function of pressure and concluded that there was no phase change up to 30 000 kg/cm^2, a conclusion which was verified by x-ray studies over a temperature range of 77° to 735°K (the melting point) by Scanlon and Lark Horovitz[5] in 1947. Many measurements have been published of the electrical resistivity and Hall coefficient as they are affected by temperature, pressure, crystal orientation, and the presence of various alloyed elements.[6–9] Measurements of the absorption and transmission of infrared light were reported by Loferski[10] and by Caldwell and Fan.[11] All electrical and optical measurements confirm that single-crystal tellurium is a semiconductor with a forbidden band about 0.34 eV in width. The structure of the allowed energy bands has been discussed by several authors.[12–14] The most recent treatment is that of Nussbaum and Hager[15] who postulate a six-ellipsoid model for each band which gives semiquantitative agreement with experiment. These physical studies form a basis for the investigation of photoconductivity in tellurium.

Intensive study of the photoconductive process in tellurium began with the work of Moss[16] in 1952. He measured photoconductive response of layers produced by vacuum evaporation as a function of wavelength and temperature and determined the limiting sensitivity and time constant. In 1955 Redfield[17] studied the process of recombination of optically excited holes and electrons in single-crystal tellurium and concluded that direct recombination was the dominant process. With the advent of better crystals produced by vapor condensation, and especially by the Czochralski technique, more accurate studies of the photoconductive process became possible. Suits[18] and Edwards[19] showed that in respect to minimum detectable energy tellurium rivalled all other detectors of energy in the region of 3.5-μ wavelengths. An important investigation by Blakemore[20] and others at the Honeywell Research Center using well-prepared, single-crystal tellurium showed a relationship between recombination velocity and mechanically produced defects and demonstrated rather conclusively that recombination via traps was the predominant mechanism, especially at low temperatures.

Studies of tellurium for nearly two centuries have led to a clear understanding of many of its chemical and physical properties, but the majority of investigations concerned with the transport of electricity have been to some extent vitiated by failure to recognize that im-

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perfections in the crystal lattice are produced by mild mechanical stress and such imperfections have a profound effect on many electrical processes in tellurium. The existence of an active crystal growing program at the Infrared Laboratory, University of Michigan, made possible the refinement of each step in the preparation to the point where the best samples show a higher degree of perfection than any previously reported. Accordingly the present results should be more nearly characteristic of the material than most of the earlier findings.

Because of the difficulty and the importance of sample preparation, the techniques used are described in some detail in the following section in which mention is also made of the apparatus and methods of measurement. In Sec. III we consider the results and the interpretation of the photoconductivity measurements.

II. TECHNIQUE

Sample Preparation

Single-crystal boules were furnished by Richard C. Keezer of the Infrared Laboratory, University of Michigan, who grew them by the Čzochralski process in a hydrogen atmosphere. The starting material was 99.999% pure tellurium obtained from the American Smelting and Refining Company. The finished boules were 5 to 10 cm long and 1 to 2 cm in diameter. The c axis of the crystal was parallel to the axis of the boule.

To prepare a sample for electrical measurements a 2.5-cm length of a boule was cut off by means of a string saw. The "string" was a 0.25-mm-diam platinum wire dipping into a solution of 3 parts 48% hydrofluoric acid, 5 parts concentrated nitric acid, and 3 parts glacial acetic acid by volume. The resulting piece of tellurium was then cleaved parallel to the axis of the boule at liquid-nitrogen temperature to minimize plastic deformation. Successive cleaving parallel to the first yielded a slab approximately 2 mm thick. A metal template having the contour desired for the finished specimen was cemented to the slab to support the tellurium and guide the cutting. The excess portions of the slab were cut away using a fine jet of compressed gas bearing abrasive particles from an S. S. White Company Airbrasive machine. The final shape was a rectangular parallelepiped 25 mm long by about 2.5 mm wide with one opposed pair of sidearms about 4 mm distant from each end. The cement holding the template was then dissolved and 0.25-mm platinum wires welded to ends of the central section and the ends of the side arms. The welding was done in a hydrogen atmosphere, enough heat being produced by electric current flowing in the wire to melt the tellurium causing it to wet the wire where the two are in contact. Such contacts are mechanically strong, Ohmic, free of excess noise, and have low resistance. The specimen was next etched in a fast acting solution (composed of 1 part 48% hydrochloric acid, 1 part chromium trioxide, and 3 parts water by weight) until the 2-mm thickness had been reduced to about 1.5 mm and the other dimensions correspondingly. Such drastic treatment removes the strained material near the surface due to the cleaving, cutting, and handling. The sample was next etched in hot, concentrated sulfuric acid to remove any residual stain and to produce a bright, smooth surface, and finally rinsed in water and then in reagent grade methanol and air dried.

The tellurium sample was mounted by cementing one end to a copper holder using General Electric Company No. 7031 Adhesive and Insulating Varnish. This style of mounting left the central part of the sample (as well as one end) out of contact with any solid material so as to avoid stress due to differential thermal expansion, etc. The use of one end wire as a handle and the cantilever mounting protect the specimen from forces greater than its own weight and thus avoid mechanical damage to the etched specimen.

Apparatus

The tellurium sample on its copper holder was mounted inside a copper box which was, in turn, clamped to the inner chamber of an evacuated double Dewar. A hole in the copper box was aligned with a sapphire window in the Dewar so that the sample could be irradiated from an external source. The outer chamber of the Dewar was filled with liquid nitrogen; the inner chamber was filled with liquid helium, nitrogen, or oxygen depending upon the temperature desired. For higher temperatures an electric heater was inserted into the inner chamber. Vacuum in the Dewar was maintained by continuous operation of a diffusion pump. Temperature was measured by a copper–Constantan thermocouple cemented inside the copper box. Copper leads were soldered to the free ends of the platinum wires in contact with the tellurium specimen and brought out through a vacuum seal in the wall of the Dewar.

In order to produce optical excitation the sample could be illuminated by radiation from a variable aperture cavity maintained accurately at 1125°K. For transient response measurements the sample could be simultaneously illuminated by a second, much weaker source which was modulated in approximately sinusoidal fashion by a variable frequency chopper. All light entered the Dewar through a filter with a wavelength pass band of 3.3 to 3.7 μ which is appropriate to excite electrons across the band gap.

In order to measure electrical conductance a high-impedance, dc source was connected to the ends of the sample and the resulting voltage measured across a pair of adjacent sidearms. The bias current was kept at 0.25 mA to avoid appreciable Joule heating. The steady component of the voltage was measured by a potentiometer and the time-varying component by a narrow-band, tunable amplifier. This amplifier consisted of a three-stage, broad-band preamplifier using 6CW4 vacuum tubes followed by a HP model 302A narrow-

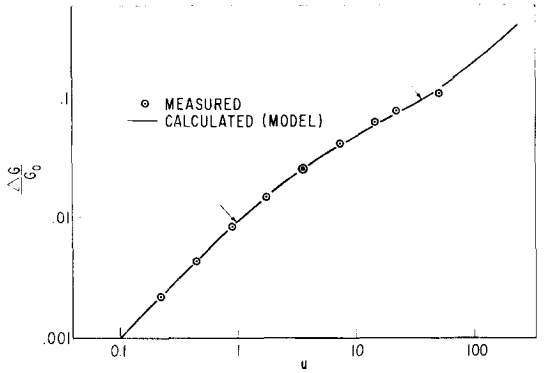

FIG. 1. Steady-state photoconductive response vs normalized illumination intensity at 77°K.

band analyzer. A 1:12 stepup transformer was used to couple the ~3000-Ω sample to the preamplifier and a blocking condenser was put between the sample and the input transformer. The output from the preamplifier was displayed on an oscilloscope and the (rectified) output from the analyzer was connected to a pen recorder through a low pass filter. A sinusoidal signal with its frequency in the pass band of the analyzer was often switched across a 1Ω resistor in series with the tellurium to calibrate the gain of the system for the existing values of input resistance, frequency, tube parameters, etc.

III. RESULTS AND INTERPRETATION

Resistivity

In the extrinsic temperature range below ~100°K tellurium is p type and the effect of all known doping agents and structural imperfections is to decrease the resistivity. Accordingly the resistivity at 77°K is a convenient and sensitive indicator of crystalline perfection. It was found that if a sample is stored in vacuum at room temperature the value of ρ_{77} increased for several months before reaching a stable value. Thus, sample No. TB-9-1 had an initial value of $\rho_{77}=41.5\Omega$ cm (parallel to the c axis) which rose to a final value of 63.0 Ω cm after 160 days. A similar increase in resistivity of tellurium has been observed by Caldwell[9] who suggested that it was caused by the annealing of strains. Keezer has suggested that the change may be due to the evolution of interstitial hydrogen incorporated during the growing process. Sample No. TB-9-1 had the highest early resistivity of any of the samples prepared in the present study and it was the only one followed to a steady value. All measurements reported in this paper were made on this sample after the drift in its resistivity had become negligible.

Hall effect measurements at 77°K show that the most carefully prepared samples have the smallest carrier density, the smallest measured values being close to 0.8×10^{14} holes/cm^3, which implies a Hall mobility of ~2000 cm^2/V sec for the holes.

Photoconductivity

In this section we shall give the results of steady-state photoconductive response measurements and the results of two types of transient response measurement. A trapping model is then analyzed which agrees to a good approximation with the observed behavior in the three cases.

Steady-State Photoconductive Response

The increase in the conductance of the sample, ΔG, above the dark value G_0 when exposed to steady illumination depends upon the intensity of the illumination as shown by the measured points in Fig. 1. It is seen that for small changes the response is proportional to the first power of the excitation but above $\Delta G/G_0=0.02$ the response increases approximately as the square root of the intensity. Similar measurements on tellurium have been reported[15,16,19] though no detailed, satisfactory mechanism has been proposed.

Transient Photoconductive Response

When the tellurium sample is illuminated by weak, sinusoidally modulated light of constant peak intensity, the amplitude of the resulting sinusoidal variations in its conductance (which were measured by the narrow band, tunable amplifier system) depends upon the modulation frequency. The measured amplitudes were closely fitted by an expression of the form $\tau^2/(1+\omega^2\tau^2)$, where $\omega=2\pi f$ is the angular frequency and τ is the responsive time constant. The value of τ was also measured by observing on an oscilloscope the exponential response to abrupt, small changes in illumination. The measured time constant depends upon the temperature of the tellurium as shown by the points in Fig. 2. It is seen that the time constant is independent of temperature below ~75°K but falls rapidly at higher temperatures. If the tellurium temperature is held constant and a source of steady illumination introduced in addition to the modulated source, it is found that the responsive time constant depends upon the intensity of

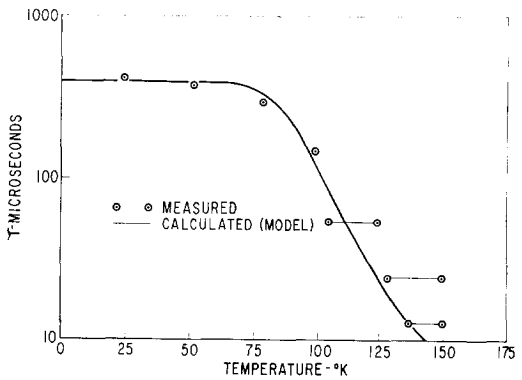

FIG. 2. Small-signal photoconductive time constant vs temperature.

the steady illumination. It is convenient to determine the intensity of the steady light by measuring the resulting steady change in the conductivity. As shown by the points in Fig. 3, the measured value of the responsive time constant is independent of optical excitation rate for low excitation but decreases sharply for higher values of excitation.

Steady-State and Transient Photoconductivity: Analysis

The observed steady-state and transient photoconductive behavior is duplicated rather accurately by the behavior of the trapping model shown in Fig. 4 where the arrows represent electron transitions.

In Fig. 4 the arrow at the left represents optical excitation of electrons from the valence band to the conduction band. The arrows at the right side of Fig. 4 represent recombination of free electrons and holes via type J traps which also capture thermally excited valence electrons. The central arrow in Fig. 4 represents either or both direct radiative recombination and recombination via traps which do not accommodate an appreciable number of excited electrons. Qualitatively the behavior of the model is as follows. The parameters are so chosen that the R pathway is a more efficient recombination mechanism than the type J traps and at low optical excitation the number of trapped electrons is large compared to the number of free electrons. As a result, most of the recombination at low excitation is carried out by the less efficient process. For sufficiently large excitation, either optical or thermal, nearly all the type J traps are occupied and, since no more electrons can be accommodated by the traps, the proportion of free electrons increases. Thus at high excitation the more efficient process dominates and a more rapid transient response ensues. The sublinear portion of the steady-state response occurs during the transition from the less efficient process to the more efficient process, the response being linear at each extreme.

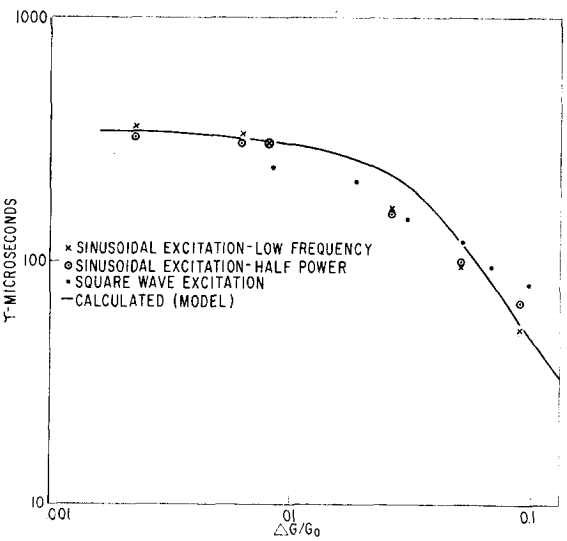

FIG. 3. Small-signal photoconductive time constant vs conductance change due to steady optical excitation.

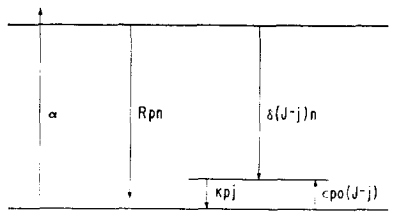

FIG. 4. A model for the steady-state and transient photoconductive behavior. α = optical excitation rate, p = density of holes in valence band, p_0 = density of holes in valence band at equilibrium, n = density of free electrons, j = density of trapped electrons, J = density of traps, R = measure of "direct" recombination probability, δ = measure of free electron trapping probability, k = measure of hole trapping probability, and ϵ = measure of hole emission probability.

To examine the behavior of the model quantitatively we first write the continuity equations neglecting any effects due to divergence of current or diffusion due to carrier concentration gradient. The result for the free and trapped electrons, respectively, is

$$dn/dt=\alpha-Rp_0n-\delta(J-j)n, \tag{1}$$

$$dj/dt=\delta(J-j)n+\epsilon p_0(J-j)-kp_0j. \tag{2}$$

In writing Eqs. (1) and (2) we have taken $p=p_0$ which is a good approximation since the largest change in conductance observed was less than 10%.

For the steady-state case the derivatives in (1) and (2) vanish and we solve the resulting algebraic equations for the increments in n and j due to optical excitation obtaining

$$\frac{\Delta n}{J}=\frac{n}{J}=\frac{u(k+\epsilon)/kD}{M+(J-j)/J}, \tag{3}$$

$$\frac{\Delta j}{J}=\frac{j}{J}\frac{\epsilon}{k+\epsilon}\approx\frac{uk/(k+\epsilon)}{u+M+k/(k+\epsilon)}, \tag{4}$$

where

$$u\equiv\alpha/(k+\epsilon)Jp_0,$$

$$M\equiv Rp_0/\delta J,$$

$$D\equiv\delta J/kp_0.$$

The relation between steady-state optical excitation and response is then found by using (3) and (4) to evaluate the fractional change in conductance, thus

$$\Delta G/G_0=(\Delta p+b\Delta n)/p_0=[\Delta j+(b+1)\Delta n]/p_0, \tag{5}$$

where b is the mobility ratio.

We find that (5) gives a good fit with the measured steady-state response as shown by the curve in Fig. 1 provided $J=0.06p_0=0.48\times10^{13}$ traps/cm^3 and provided that the low excitation value of $\Delta j/\Delta n\approx6$.

To investigate the transient behavior of the model we use Eqs. (1) and (2) without restriction on the value of

the derivatives and rewrite the variables in terms of small perturbations about average values, thus

$$\begin{aligned} \alpha &= \alpha_0 + \alpha(t), \\ n &= n_0 + \Delta n, \\ j &= j_0 + \Delta j. \end{aligned} \tag{6}$$

Neglecting higher powers of the increments gives

$$d(\Delta n)/dt = a_{11}\Delta n + a_{12}\Delta j + \alpha(t), \tag{7}$$

$$d(\Delta j)/dt = a_{21}\Delta n + a_{22}\Delta j, \tag{8}$$

where

$$\begin{aligned} a_{11} &= -Rp_0 - \delta(J-j), \\ a_{12} &= \delta n, \\ a_{21} &= \delta(J-j), \\ a_{22} &= -\delta n - (\epsilon + k)p_0. \end{aligned} \tag{9}$$

The solutions of (7) and (8) are linear combinations of two exponential terms, the time constants being the roots of the characteristic equation

$$(1/\tau)^2 + B(1/\tau) + C = 0, \tag{10}$$

where

$$\begin{aligned} B &= a_{11} + a_{22}, \\ C &= -a_{12}a_{21} + a_{11}a_{22}. \end{aligned}$$

The roots of (10) are approximately

$$1/\tau_1 = -B = -a_{11} - a_{22}, \tag{11}$$

$$1/\tau_2 = -C/B = (a_{12}a_{21} - a_{11}a_{22})/(a_{11} + a_{22}). \tag{12}$$

Upon evaluating (11) and (12) by means (9) and investigating the dependence of τ_1 and τ_2 on excitation we find that τ_2 agrees well with the behavior of the observed responsive time constant while τ_1 does not. We conclude that τ_1 corresponds to a faster process which was not detectable by the measuring techniques used.

After some experimentation it is found that τ_2 fits the observed values as shown by the curves in Figs. 2 and 3 provided we take $R = 0.56 \times 10^{-8}$, $\delta = 1.85 \times 10^{-8}$, $k = 0.31 \times 10^{-6}$, $\epsilon/k = 20T^{\frac{3}{2}} \exp(E/KT)$, and $E = 0.072$ eV above valence band.

We may regard δ as the product of an average trapping cross section for electrons and an average thermal velocity v. Taking $v = 5 \times 10^6$ cm/sec at 77°K we find

$$S_n = \delta/v = 0.4 \times 10^{-14} \text{ cm}^2.$$

Similarly for k we have

$$S_p = k/v = 0.6 \times 10^{-17} \text{ cm}^2.$$

For consistency we must assume that when a trap is unoccupied by an electron (and therefore ready to trap one) it has a unit positive charge and when it is occupied (and therefore ready to trap a hole) it is neutral. The values of S_n and S_p above are within the range of 10^{-12} to 10^{-22} cm^2 given by Bube[21] but are smaller by a factor of 100 than the typical values quoted for attracting and neutral centers, respectively.

The present model resembles one suggested by Blakemore *et al.*[22] to account for a different type of photoconductivity experiment in tellurium which also postulated a set of traps competing with a more vigorous recombination mechanism. However, the model of Blakemore *et al.* required an "implausibly large trap density" (2×10^{16} cm^{-3}) having trap energy level near the top of the gap, while the present model requires 0.5×10^{13} traps/cm^3 with energy levels near the bottom of the gap.

Since the exciting radiation is absorbed in traversing a 1.5-mm-thick section of tellurium, the excitation and the carrier concentration are not completely uniform. This complication and others are ignored in the simple treatment given here and only approximate agreement between the model and the observed photoconductive behavior is expected. To this degree of approximation the trapping model presented here gives a comprehensive view of the photoconductive process in extrinsic tellurium. No explanation of the physical structure of the traps can be given at present; such understanding must await further investigation of this difficult material.

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