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LONG WAVELENGTH PHOTOEFFECTS IN MERCURY SELENIDE, MERCURY TELLURIDE, AND MERCURY TELLURIDE-CADMIUM TELLURIDE*

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Abstract—Mercury selenide, mercury telluride, and mercury telluride–cadmium telluride are semiconductors which have been investigated as intrinsic infrared detecting materials. Mercury selenide and mercury telluride in the photoelectromagnetic–Nernst configuration exhibit spectral and frequency responses indicative of thermal rather than photon behavior. The signal is believed due to the Nernst thermal effect rather than the PEM photon effect. Mercury telluride–cadmium telluride exhibits photoconductivity at 77°K and 4.2°K with a spectral response extending past 15 μ .

INTRODUCTION

MERCURY selenide and mercury telluride are IIB-VIA compound semiconductors having narrow energy gaps which are being investigated as intrinsic photon detecting materials for long wavelength infrared radiation. The direct gap of HgSe has been reported to be 0.12 eV by Zhuse, ⁽¹⁾ although Strauss and Harman⁽²⁾ suggest it is a semimetal with a band overlap of 0.1 eV. Wright *et al.* ⁽³⁾ indicate it has a direct gap of 0.2 eV, whereas Blue and Kruse⁽⁴⁾ find the gap to be equal to or greater than approximately 0.10 eV. Optical studies at Battelle Memorial Institute⁽⁵⁾ show the absorption edge to lie in the $10-15 \mu$ interval and to be dependent upon carrier concentration.

The direct gap of HgTe is smaller than that of HgSe. Harman *et al.* ⁽⁶⁾ find it to be 0.02 eV, whereas Carlson⁽⁷⁾ and Black *et al.* ⁽⁸⁾ report it to be 0.025 eV. Nelson⁽⁹⁾ reports it at slightly less than 0.01 eV. The value of 0.02 eV corresponds to a long wavelength limit of 62 μ .

Mercury telluride alloyed with cadmium telluride is a semiconductor having an energy gap dependent upon the relative amounts of cadmium telluride and mercury telluride. Lawson *et al.* ⁽¹⁰⁾ indicate the gap increases monotonically with increasing relative amounts of CdTe. An alloy of 90 per cent mercury telluride-10 per cent cadmium telluride was reported to have a gap of 0.1 eV, corresponding to a long wavelength limit of about 12 μ .

MATERIAL PREPARATION

HgSe and HgTe are prepared by direct reaction of the elements in evacuated thick-walled quartz capsules. Because the vapor pressure of free Hg at the melting point of HgSe is over 100 atm, explosions are frequent. Explosions of HgTe, which has a melting point of 670°C, are less frequent. Ingots of HgSe and HgTe are prepared by slowly heating the capsules containing the elements at temperatures well below the compound melting point until the

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reaction has occurred and little or no free Hg exists. The capsules are then heated to approximately 30°C above the compound melting points and slowly lowered through a Bridgman furnace. The ingots so formed are polycrystalline with average crystallite sizes of the order of 5 mm. Hall and resistivity measurements over the interval from 77°K to 300°K indicate the HgSe to be invariably *n*-type, whereas all HgTe ingots prepared to date have been *p*-type. The purity, of the order of 10^{17} - 10^{18} cm⁻³, is believed to be controlled by deviations from stoichiometry; the HgSe containing excess Hg atoms either interstitially or due to vacancies in the Se sublattice, and the HgTe containing excess Te atoms, either interstitially or due to vacancies in the Hg sublattice.

Mercury telluride–cadmium telluride is prepared from ingots of HgTe and CdTe. Proper proportions of HgTe and CdTe in an evacuated quartz capsule are lowered through a Bridgman furnace. Most ingots have been made from 10 at. per cent CdTe and 90 at. per cent HgTe. Because the CdTe segregates from the HgTe during freezing, the composition along the ingot is nonuniform. Hall measurements to $4 \cdot 2^{\circ}$ K indicate the ingots to be *n*-type with a purity in the 10^{15} cm⁻³ range.

PHOTON vs. THERMAL EFFECTS

Construction and evaluation of HgSe, HgTe, and HgTe-CdTe detectors have been undertaken. The measurement geometries are those of the photoelectromagnetic (PEM) effect, and the photoconductive effect, see Fig. 1. In each of the geometries a thermal effect



FIG. 1. Sample geometries: (a) PEM-Nernst effect, (b) photocondcutive-bolometer effect.

competes with a photon effect. In the photoconductive geometry the bolometer effect competes with photoconductivity whereas in the PEM geometry the Nernst effect competes with the PEM effect. It will be seen that the measurements reported here indicate that the thermal effects dominate in HgSe and HgTe for the available sample purities.

Long wavelength photoeffects

Becker and Sochard ⁽¹¹⁾ have investigated the relationships between the thermal and photon effects for an intrinsic semiconductor, and evaluated them for Mg₂Sn, which has an energy gap of 0.33 eV. For a semiconductor having a forbidden gap E_g , an intrinsic concentration p_i , an ambipolar diffusion length L_D , a specific heat C_p , a density d, a lifetime τ , and a thermal conductivity K, the ratio of the a.c. Nernst short circuit current I_N to the PEM short circuit current I_{PEM} is

$$\frac{I_N/B}{I_{\text{PEM}}/B} = \frac{E_g h_V p_i \left(l + s_o L/D\right) D^{\frac{1}{2}}}{2kT^2 \left(C_v dK\omega\right)^{\frac{1}{2}\tau^{\frac{1}{2}}}},\tag{1}$$

where s_o is the front surface recombination velocity, D is the diffusion constant, ω is the angular frequency, B is the magnetic induction, and the remaining symbols have their usual significance.

From Equation (1) it can be seen that the thermal effect will dominate the photon effect at large intrinsic concentrations. Since p_i is exponentially dependent upon E_g , this means that the thermal effect tends to dominate the photon effect in narrow gap semiconductors. At low frequencies the Nernst effect falls off with the square root of the frequency whereas the PEM effect is frequency independent. For samples with small front surface recombination velocities, an increase in material lifetime will increase the PEM signal relative to the Nernst signal.

Similar considerations apply to the relationship between the bolometer and photoconductive effects. The ratio of the bolometer conductance change ΔG_B to the photoconductive conductance change ΔG_{PC} is

$$\frac{\Delta G_B}{\Delta G_{PC}} = \frac{E_g h v p_i \left(l + s_o L/D \right)}{2k T^2 C_g d \omega \tau}.$$
(2)

Again, because of the exponential dependence of concentration upon energy gap, the thermal effect tends to dominate the photon effect in narrow gap semiconductors. At low frequencies the bolometer effect varies inversely with frequency whereas the photoconductive effect is frequency independent. Long lifetimes will favor the photoconductive signal over the bolometer signal.

DETECTOR CONSTRUCTION AND EVALUATION

Detectors have been prepared from HgSe and HgTe ingots for evaluation in both configurations, and from HgTe-CdTe in the photoconductive configuration only. Samples sliced from the ingots were lapped to a thickness of 0.005 in. Both front and back surfaces were etched to provide low recombination velocities in the photoconductive-bolometer geometry, whereas the front was etched and the back lapped in the PEM-Nernst geometry. Final thicknesses for both sample configurations were 10-25 μ . PEM-Nernst geometry elements were mounted in a standard Honeywell PEM envelope having a field strength of 10 kG. Measurements were made at room temperature only. The photoconductivebolometer geometry elements were mounted in a demountable helium Dewar flask. Measurements were made at 295, 77, and $4\cdot2^{\circ}K$.

Mercury selenide samples exhibited a photosignal in the PEM-Nernst configuration. (12)

No signals were obtained in the photoconductive-bolometer configuration at either 295 or 77° K. Measurements were not attempted for HgSe at 4.2° K.

The value of $D^*(500^{\circ}\text{K}, 400, 1)$ for HgSe detector 6A-223 in the PEM-Nernst configuration was 1.3×10^6 cm cps⁴/W. The spectral response for equal power input per unit wavelength interval for the detector is shown in Fig. 2. It is apparent that the response is not typical of a photon detector. First, the response is wavelength independent from 3 to 15μ rather than increasing with wavelength. Second, the response does not exhibit a long wavelength limit in the interval from 12 to 15μ corresponding to the energy gap of HgSe. Third, a peak exists at 0.6μ .

Figure 2 also shows the spectral response for equal power input per unit wavelength



FIG. 2. Spectral responses of HgSe detector 6A-223 and HgTe detector 6A-282.



FIG. 3. Frequency response of HgSe detector 6A-223 and HgTe detector 6A-282.



FIG. 4. Spectral response of HgTe-CdTe detector PC-1 at $77^\circ K$ and $4{\cdot}2^\circ K.$



FIG. 5. Frequency response of HgTe-CdTe detector PC-1 at 77°K and 4.2°K.

interval for HgTe PEM-Nernst detector 6A-282. Here the response increases with wavelength in the interval from 5 to 22μ but decreases with increasing wavelength from 2 to 4μ . Since the absorption edge of HgTe should lie at about 62μ , it would be desirable to extend the measurements to that point, but insufficient source power at longer wavelengths prevented this.

The frequency response of the HgSe detector is shown in Fig. 3. It is not the response expected from a photon detector, since it begins to fall off with increasing frequency below 100 c/s. The frequency response of the HgTe detector shown in Fig. 3 also falls with increasing frequency, which is not characteristic of a photon detector.

The spectral response and frequency response of the HgSe detector indicate it to be operating in the Nernst mode. The peak at 0.6μ remains unexplained. The possibility that a second phase exists, such as a free phase of selenium, was explored with negative results. Frequency response measurements for monochromatic 0.6μ and 3μ radiation were identical, indicating that the thermal mechanism responsible for the 0.6μ peak was the same as that for the longer wavelength behaviour.

The frequency response of the HgTe detector indicates that it too operates in the Nernst mode. Although the spectral response was not wavelength independent, it was not that of a photon counter. The variation with wavelength probably represents the variation with wavelength of the absorbing mechanism. Although Becker and Sochard⁽¹¹⁾ based their theory on an intrinsic absorption mechanism, the behavior in HgSe and HgTe indicates that an absorbing film or damaged surface layers are more probably responsible.

Although no signals were detected for HgSe in the photoconductive-bolometer configuration, they were found in HgTe at 295, 77, and $4\cdot 2^{\circ}$ K. From frequency response measurements at all three temperatures, it appears that a thermal mode of operation was observed.



FIG. 6. Noise spectra of HgTe-CdTe detector PC-1 at 77°K and 4.2°K.

However, no spectral response measurements were made, so photoconductive behavior in HgTe has not been completely ruled out.

The spectral response of HgTe-CdTe detector PC-1 in the photoconductive-bolometer configuration at 77 and $4\cdot 2^{\circ}$ K is shown in Fig. 4. Two signals at each temperature are observed, depending upon the direction of the bias current. For both temperatures the signal increases with wavelength, indicating photon counting behavior. The frequency response is shown in Fig. 5. For monochromatic 10 μ radiation the signal is independent of frequency to 800 c/s at both temperatures. However, for 2 μ radiation, the signal at $4\cdot 2^{\circ}$ K decreases with increasing frequency to about 400 c/s, where it begins to level off. From Fig. 4 it can be seen that at $4\cdot 2^{\circ}$ K in the region from 2 to 4 μ the signal is independent of wavelength. Thus the spectral response and frequency response curves together indicate that at $4\cdot 2^{\circ}$ K a thermal effect, the bolometer effect, is dominant at short wavelengths, whereas photoconductivity is dominant at long wavelengths.

The noise spectra for detector PC-1 at 4.2 and 77° K are shown in Fig. 6. Current noise appears to be dominant over the frequency range indicated. The dependence of signal,



FIG. 7. Signal, noise, and signal-to-noise ratio as functions of bias current for HgTe-CdTe detector PC-1 at 77° K and $4\cdot 2^{\circ}$ K.

noise, and signal-to-noise ratio upon bias current at 4.2° K for 500°K source radiation is shown in Fig. 7. Note that the signal increases linearly with bias at low currents, but tends to saturate at high currents. The noise rises with increasing current, as would be expected from current noise. The signal-to-noise ratio therefore exhibits a maximum. Evaluation of D^* (500°K, 400, 1) at the maximum at 4.2° K indicates a value of 1.1×10^7 cm cps³/W. The value of D^* at 77°K is approximately 10 times poorer.

CONCLUSIONS

Photosignals observed in the PEM-Nernst configuration for the narrow gap semiconductors HgSe and HgTe are of thermal rather than photon origin. This bears out theory which indicates the thermal effects tend to dominate in materials with large intrinsic concentrations, i.e., small energy gaps. If the materials were sufficiently pure, then cooling would greatly reduce the intrinsic concentration and cause the photon effects to dominate. Because the HgTe and HgSe are highly impure due to stoichiometric deviations, cooling does not cause the photon effects to dominate.

An alloy of 90 per cent HgTe-10 per cent CdTe exhibits photoconductivity at 77 and $4\cdot 2^{\circ}$ K for wavelengths past 4 μ . At 2 μ a bolometer rather than a photoconductive signal is observed at $4\cdot 2^{\circ}$ K for frequencies below 800 c/s. Current noise limits the value of D^* (500°K, 400, 1) to the 10⁶-10⁷ cm cps¹/W range.

REFERENCES

- 1. ZHUSE, V. P., J. Tech. Phys., Moscow 25, 2079 (1955).
- STRAUSS, A. J., and T. C. HARMAN, Bull. Amer. Phys. Soc. Series II, 6, 155 (1961); Conference on Semiconducting Compounds, Schenectady (June 14-16, 1961), paper E5.
- 3. WRIGHT, G. B., A. J. STRAUSS, and T. C. HARMAN, Bull. Amer. Phys. Soc. Series II, 6, 155 (1961).
- 4. BLUE, M. D., and P. W. KRUSE, J. Phys. Chem. Solids, to be published.
- 5. Communication from T. S. SHILLIDAY, Battelle Memorial Institute.
- 6. HARMAN, T. C., M. J. LOGAN, and H. L. GOERING, J. Phys. Chem. Solids, 7, 228 (1958).
- 7. CARLSON, R. O., Phys. Rev. 111, 476 (1958).
- 8. BLACK, J., S. M. KU, and H. T. MINDEN, J. Electrochem. Soc. 105, 723 (1958).
- 9. NELSON, R. E., Sc. D. thesis, Massachusetts Institute of Technology (1961).
- 10. LAWSON, W. D., et al., J. Phys. Chem. Solids 9, 325 (1959).
- 11. BECKER, J. H., and I. I. SOCHARD, NBS Report No. 6437 (June 1959); Bull. Amer. Phys. Soc. 3, 114 (1958); BECKER, J. H., J. Appl. Phys. 31, 612 (1960).
- 12. BLUE, M. D., J. H. GARFUNKEL, and P. W. KRUSE, J. Opt. Soc. Amer. 51, 1408 (1961).