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## II. APPLICATIONS OF CADMIUM TELLURIDE AND DEVICES BASED ON THIS MATERIAL.

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### Section II.1 : CdTe nuclear detectors.

#### a) General properties.

### APPLICATIONS OF CdTe. A REVIEW

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**Résumé.** — Cet article de synthèse retrace tout d'abord l'évolution historique du tellure de cadmium, puis il considère les applications potentielles ainsi que les limitations de ce matériau composé. Certaines propriétés physiques du tellure de cadmium rendent ce matériau particulièrement intéressant pour la réalisation de dispositifs électroniques et surtout optoélectroniques. Par ailleurs, la possibilité d'obtention de films minces à partir de matériaux de faible prix présente des avantages de coût sur d'autres dispositifs. Les principaux freins à son emploi peuvent être classés en trois groupes :

- 1) Manque de contrôle de la durée de vie des porteurs minoritaires ;
- 2) Propriétés et performances des couches minces non reproductibles ;
- 3) Manque de bons contacts ohmiques sur les cristaux p de faible résistivité.

Quelques suggestions d'études à entreprendre dans ces domaines sont également données.

**Abstract.** — The review considers the history of CdTe in short form and delineates the applications potential for the compound.

This potential is seen to arise on the one hand from a combination of various physical properties which is useful for several classes of electronic and particularly optoelectronic devices, and on the other hand from the fact that thin film fabrication and low cost starting materials could give it significant cost advantages over other semiconductors. The obvious lack of widespread application is traced to three fundamental problems :

- 1) Lack of control over minority carrier behavior ;
- 2) Erratic and non reproducible performance of thin films ;
- 3) Lack of good contacts to low resistivity p-type material.

Some suggestions on further work in these areas are also advanced.

**1. Introduction.** — Cadmium telluride has been known as a compound for  $\sim 100$  years. In 1879 it was prepared along with many other tellurides in France by the chemist Margottet, who reacted *Te with the metals at red heat*. As reported subsequently by Fabre [1] who determined the heat of formation of the compound in 1888, this process leads to well-crystallized material. Thus we can see that ease of preparation has been a hallmark of CdTe from the very beginning and the basic method of preparation has changed little to this day. Tibbals [2] in 1909 reports on another investigation of tellurides, among them CdTe. The Te he used was obtained from the *Baltimore Copper Rolling and Smelting Co.*, which extracted it from electrolytic slimes. Virtually all Te is still obtained in this way today.

Although tellurides were of some intermittent interest to chemists and mineralogists, the only apparent use of CdTe reported up to the 1940's was as a pigment [3]. In 1946, however, Frerichs and Warminsky [4, 5] reported that *Incomplete Phosphors*,

such as the chalcogenides of Cd, in thin film form were highly photosensitive to a range of photon energies including  $\beta$  and  $\gamma$  radiation. They ventured the suggestion that the effect could be used for the fabrication of  $\gamma$ -ray image converter tubes, or if combined with suitably efficient amplifiers, in  $\gamma$ -quantum counters.

By 1948 photocells of CdTe were already being built [6, 7] and it was noted that preparative and heat treatment conditions as well as stoichiometric excesses of either kind were of great influence in the functioning of these devices. In the 1950's several detailed investigations of the behavior of CdTe single crystals were made [8-10], in particular, Kroeger and de Nobel [11] and Boltaks, Konorov and Matveev [12] did detailed doping studies which established the basis for various uses of the compound. Finally in 1959 de Nobel's [13] thesis appeared. It not only described the behavior of the compound in great detail, but also explained the behavior of the dopants in terms of a coherent model. Thus, the stage was

set for the application of the compound in a variety of devices. In a patent filed in 1959 [14] de Nobel and Kroeger remarked :

« As is well known, cadmium-telluride is a semiconductor which has very advantageous properties as compared to the other semiconductor chalcogenides of cadmium, such as comparatively great mobility, a simple controllability of the conductivity from n- to p-type, and conversely, so that cadmium telluride may be used in semiconductor devices such as crystal diodes or transistors. It is also known that cadmium telluride is photosensitive to many kinds of radiation, for example, to infrared and visible radiation and X-radiation, so that it may be used in photosensitive devices such, for example, as photodiodes, or as photoconductive bodies or infrared telescopes, image intensifiers, camera tubes and photo-electric cells, X-ray dosimeters and the like. »

Obviously that was already a quite promising list, to which more application possibilities had already been or would soon be added.

In summary, by 1960 all the desirable properties of CdTe, including its easy fabricability in thin film form were well known ; thus it entered the 60's with high promise for all kinds of applications, the major groups of which are noted below.

However, before I get into these, I should note that the references given are not always complete, and the reader must further refer to the reference lists of each of the references mentioned to obtain a complete picture with respect to each of the applications. In particular, I wish to apologize to those inventors who had their good ideas earlier than the people whom I have named in this review, but it turned out to be a practical impossibility to track down a complete chronology for each of the cited applications.

**2. Application potential.** — In this section, I have summarized the main applications of CdTe, proceeding from the more passive modes of useage to the more active ones, culminating in some quite sophisticated suggestions for thin film devices.

**2.1 INFRARED WINDOWS.** — Irtran 6<sup>(R)</sup> made by Eastman Kodak as one of their well known series of infrared transmissive materials is, of course, constituted of hot pressed CdTe. Various of its properties have been described [15, 16, 17]. Also with the advent of single crystal CdTe, many of the optical properties have been much improved and single crystal windows are now commercially available [18]. More recently CdTe has been discussed as a material for very high power CO<sub>2</sub> laser windows [19] and it indeed has potential in this area, although its low thermal conductivity as well as low mechanical strength make it imperative that it be prepared with extremely low absorption at 10.6 μ. An in-depth review of the problems and tradeoffs in the very high power laser

window field has recently been published by Deutsch [20]. Also in a later paper in this symposium, some of the problems will be treated in more detail by Bell [21]. It is quite clear, though, that the extremely flat transmission from the band edge to ~ 30 μ (Fig. 1) is not easily matched by any other

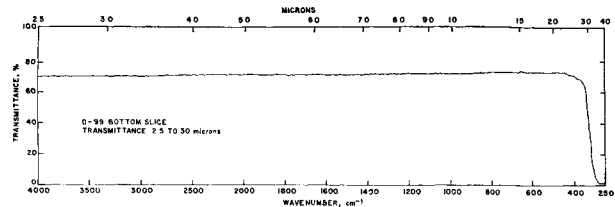


FIG. 1. — Optical transmission on a polished section of CdTe between 2.5 and 40 μ. (This was a piece 10 cm long and 2.5 cm in diameter prepared by Bridgman growth at Tyco in 1972 for window/modulator purposes. The optical absorption coefficient at 10.6 μ, measured by CO<sub>2</sub>-laser calorimetry was 0.004 cm<sup>-1</sup>.)

material of equal resistance to chemical attack. Thus, this area should always present good applications potential for CdTe as long as there exists a significant market for infrared systems.

## 2.2 ELECTRO-OPTIC MODULATOR/NON-LINEAR OPTICS.

One important application of CdTe will most certainly be as an electro-optic modulator in both the near and the far infrared. Because CdTe is a semiconductor with an energy gap of 1.5 eV, it is opaque in the visible range of the spectrum, but as noted before it does have a low absorption coefficient from its band edge at ~ 0.9 μ to ~ 30 μ which is near the edge of the reststrahl band. The fundamental lattice vibration frequency is located at 141 cm<sup>-1</sup> (70 μ).

Of great interest too is the large (relative to GaAs and other III-V semiconductors) electro-optic coefficient [22, 23]. CdTe has the zincblende (43 m) structure so it lacks a center of symmetry. The maximum phase retardation will be for light propagating along the (110) direction, polarized in the (100), with the electric field in the other (110) direction.

Table I, taken mostly from J. E. Kiefer and A. Yariv [24], is a comparison of the important electro-optic characteristics of GaAs and CdTe at 10.6 μ. In addition to the larger electro-optic coefficient, CdTe's optical absorption coefficient is less than GaAs — probably because the fundamental lattice vibration wavelength of 70 μ in CdTe is further away from the frequency of interest than the 40 μ fundamental of GaAs.

In order to be useful for any modulation, the CdTe must be of high optical quality with no inclusions, few impurities, and very little strain so that no birefringence, scattering or absorption is introduced. Single crystals must be available with reasonable dimensions (the order of centimeters is adequate for many applications) and homogeneous. A very high resistivity is also necessary to eliminate ohmic losses and free carrier absorption. It is also desirable

TABLE I  
Some characteristics of CdTe and GaAs at 10.6 μ [24]

	CdTe	GaAs
Refractive index $n_0$	2.6	3.3
$n_0^3 r_{41}$ (m/V)	$12 \pm 1 \times 10^{-11}$	$5.8 \times 10^{-11}$
Unclamped electro-optic coefficient $r_{41}$ (m/V)	$6.8 \times 10^{-12}$	$1.6 \times 10^{-12}$
Absorption coefficient $a$ , $\text{cm}^{-1}$	$0.005 \pm 0.002$	0.012-0.02
$a/n_0^3 r_{41}$ , $10^{-10}$ (V/m <sup>2</sup> )	0.5	2
Temperature coefficient of the refractive index $\frac{1}{n} \frac{dn}{dt}$ °C <sup>-1</sup>	$+ 4.4 \pm 0.3 \times 10^{-5}$	$5.67 \pm 0.34 \times 10^{-5}$
Transmission range, μ	1-30	1-18

to obtain the low carrier concentration by removal of most of the electrically active impurities rather than by significant and uncontrolled compensation. All of these important parameters have already been achieved in CdTe crystals grown in various laboratories, and CdTe modulators, just like IR windows, are commercially available today [18].

Optical mixing [25] and continuous second harmonic generation [26] using CdTe have also been demonstrated, and finally the Franz-Keldysh effect has been used for modulation in the very near infrared using 1 μ thick CdTe films [27].

Obviously then, if the market for infrared laser systems were in fact to materialize, CdTe would have an important role to play. However, that market is still of quite small size so that the infrared applications today appear market limited rather than technology limited.

2.3 GUNN EFFECT. — CdTe, like GaAs, exhibits the Gunn effect; that is, above a certain threshold applied field, high frequency current oscillations are produced [28].

GaAs Gunn diodes made from a considerable resistivity range of material have been operated with long pulses or continuous wave at average fields up to several times the threshold value of 3 kV/cm. CdTe is in many ways comparable to GaAs, particularly in that the maximum efficiency should be approximately the same for both materials as the spike amplitude for both is approximately 50 % of the maximum current [29] (Table II). However, CdTe does suffer in comparison to GaAs in two

areas — threshold voltage and carrier ionization. The threshold voltage for CdTe is approximately 15 kV/cm [29, 30] vs. 3 kV/cm for GaAs. Combined with the low thermal conductivity of CdTe, this threshold voltage implies that continuous wave CdTe Gunn diodes are unlikely. However, for short pulse operation where heat dissipation can occur in the diode, CdTe could be used. The problem of carrier ionization is also far more severe in CdTe than in GaAs [31, 32]. Whether this reflects the less advanced technology of CdTe or is an intrinsic material property cannot be said at this time.

Due to the higher threshold voltage, application in this area looks quite unpromising in comparison with GaAs though, irrespective of whether improvements in carrier ionization properties would be achieved or not. It therefore appears at present unlikely that CdTe has any advantage when used in devices which employ the Gunn effect.

2.4 PIEZOELECTRIC AND SIMILAR DEVICES. — Although CdTe is a piezoelectric semiconductor and a variety of its basic constants have been determined [33, 34] (Table III) it apparently has not been applied in this area.

However, according to Bell [35], White [36] showed that the ultrasonic gain,  $\alpha$ , for an acoustic wave is given by

$$\alpha = \frac{K^2}{2} \frac{\omega_c}{v_\gamma} \left[ 1 + \frac{\omega_c^2}{\gamma^2 \omega^2} \left( 1 + \frac{\omega^2}{\omega_c \omega_d} \right)^2 \right]^{-1}$$

$$\gamma = 1 - \frac{\mu E}{V}$$

TABLE II  
Comparison of Gunn effect parameters [29]

Material	Characteristic fields (kV/cm)			domain velocity (cm/s)	Peak-to-valley Current-ratio
	Threshold	Outside domain	Inside Domain		
CdTe	$15 \pm 2$	$7 \pm 2$	$\approx 37$	$7 \times 10^6$	$\lesssim 2 : 1$
GaAs	3	1.5	$\approx 60$	$8 \times 10^6$	$\sim 2 : 1$

TABLE III  
Piezoelectric, elastic and dielectric constants  
of cubic CdTe [33]

	- 196 °C	25 °C	Accuracy (± %)
$S_{11}$	3.83		1.5
$S_{12}$	- 1.58		1.5
$S_{44} E$	5.11		1.5
$S_{44} D$	5.11		1.5
$C_{11}$	6.15	5.351	
$C_{12}$	4.30	3.681	
$C_{44} E$	1.96	1.994	
$C_{44} D$	1.96		
$\epsilon_{11} T/E_0$	9.65		2.0
$\epsilon_{11} S/E_0$	9.65		2.0
$d_{14}$	1.68		5.0
$e_{14}$	0.033 5		6.0
$k_{14}$	0.026		4.0

$S$  is in  $10^{-11}$  m<sup>2</sup>/N.

$C$  is in  $10^{10}$  N/m<sup>2</sup>.

$d$  is in  $10^{-2}$  C/N.

$\epsilon$  is in C/m<sup>2</sup>.

$K$  is the piezoelectric coupling coefficient,  $v$  is the sonic velocity,  $\omega_c$  is the dielectric relaxation frequency ;  $\omega_d$  is the diffusion frequency,  $\omega$  is the radial frequency,  $\mu$  is the mobility and  $E$  is the applied electric field.

At first glance, it would seem that one would want a material with as large a value of  $K$  as possible to give the maximum gain, but when numbers are inserted into the expression, we find that gains such as 100 dB/mm or larger are possible in CdS. It is this extremely large acoustic amplification which makes operation without oscillation or saturation effects so difficult if delays of several microseconds are of interest.

Non-linear effects become important at a power density,  $P$ , of approximately

$$P = \frac{1}{16 \pi^2} \frac{v^3}{\mu^2 K^2} \epsilon$$

$\epsilon$  is the dielectric constant. For a shear wave in CdS this is a power of only 5 mW/cm<sup>2</sup>. Note the inverse dependence on  $K^2$ ,

Another big disadvantage of CdS and other materials is the difficulty of control of the conductivity,  $\sigma$ , since the dielectric relaxation frequency  $\sim \omega_c = \sigma/\epsilon$ . One finds that resistivities in the range of  $10^3$   $\Omega$ -cm are necessary for amplification in the 100 MHz range. The only way such resistivities may be obtained in CdS is by illumination, using the induced photoconductivity which, although it is convenient in the laboratory, does not give very uniform conductivity or lend itself to any practical device.

We feel that CdTe should be able to find a useful role in this area of piezoelectric semiconductor delay lines. For a zinblende (cubic) structure, a longitudinal

wave propagating in the (111) direction is piezoelectrically active and also a shear wave in the (110) direction polarized along a (100) axis. Its coupling coefficient of  $k \approx 0.03$  is about equal to GaAs, and only one-fifth that of CdS, but it is still large enough to give usable but not excessive ultrasonic gains. The electronic mobility of 1 100 cm<sup>2</sup>/V-s is about three times that of CdS. Ultrasonic velocities are not much different in CdS and CdTe. CdTe crystals are available with dimensions the order of centimeters and what is most important, precise control of the conductivity is possible. The one significant parameter that has not been measured, to the best of our knowledge, is the ultrasonic attenuation.

Solid state *travelling wave amplifiers* and other delay line devices are extremely important components of modern radar systems. Accordingly, the possibilities inherent in CdTe should be pursued.

2.5 LUMINESCENCE. — CdTe has by now a significant history as a material for electroluminescent diodes [37-43] and work is going on in this area at present, particularly in Japan. In general all these investigations showed two important emissions (Fig. 2) : (1) a roughly band-to-band emission into

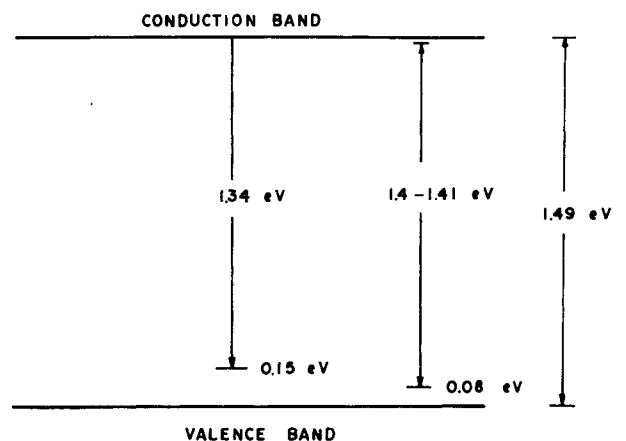


FIG. 2. — Band scheme for major emissions found in CdTe electroluminescent diodes. (These emissions are due to many authors which find them approximately at the energy levels indicated. The two level emission is also repeated in CdTe-ZnTe and CdTe-MgTe alloys which, however, now emit in the visible.)

a shallow acceptor and (2) one into an  $\sim 0.15$  eV acceptor level. Both of these, therefore, lie in the infrared. To shift the luminescence into the visible, alloying with ZnTe [44] and particularly MgTe [45-47] has been successful and by further alloying of CdTe-MgTe with Se the luminescence was shifted far out into the green at 540 nm [48].

In all these solid solutions the general mechanism of the recombination appeared to be the same as in pure CdTe, namely an emission at two wavelengths, one close to the bandgap energy and another one of the order of 10 % less than bandgap energy.

In all cases too, a drastic reduction in luminescent

efficiency occurs between liquid nitrogen and room temperature. Whereas at 77 K external quantum efficiencies of > 10 % are the rule, only fractional % are observed at room temperature. This behavior is attributed to *killer* centers near the middle of the gap. In most of these cases also, lasing was tried but not achieved due to high contact resistance on the p-type side.

Light stimulated emission [49] and electron beam stimulated emission [50] has also been observed as well as recombination radiation [51] at high bias levels. It appears then that CdTe and its alloys could have significant application as electroluminescent materials in competition with GaAs and other III-V's, if indeed the *killer* and contact problems could be overcome.

2.6 SOLAR CELLS. — In 1957 Loferski [52] published his paper on the optimal properties for a good solar cell material, which clearly demonstrated that semiconductors with bandgaps close to 1.5 to 1.6 eV would have the highest solar conversion efficiencies.

Ever since, interest in CdTe solar cells has been high. In addition to its near ideal bandgap, CdTe has a high optical absorption coefficient, which we have recently redetermined and found to be even higher than found previously [53] (Fig. 3), and thus < 2 μ of CdTe would be capable of absorbing all the usable energy from the solar spectrum. If one couples this with the high predicted conversion efficiency and the apparent ease with which CdTe

films can be made, it is quite clear that significant interest in this application would result, and an appreciable amount of work has therefore been directed towards CdTe solar cells [54-59]. However, the high efficiency predicted by Loferski has not even been closely approached ; in fact ~ 25 % of theoretical efficiency were about the best values achieved experimentally [60, 61].

To appreciate why, it serves as a good start to consider figure 4 taken from Loferski's paper. It

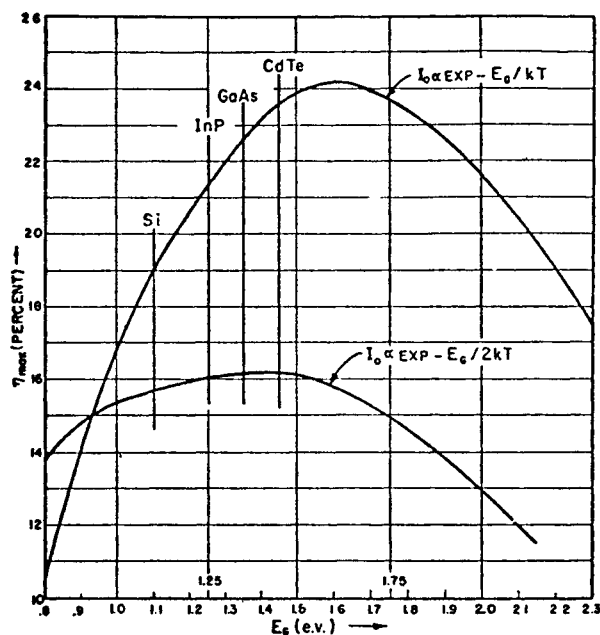


FIG. 4. —  $\eta_{max}$  vs.  $E_g$  outside atmosphere ( $m = 0, W = 0$ ) showing the effect of relation between  $I_0$  and  $E_g$ . From Loferski (Ref. [52]).

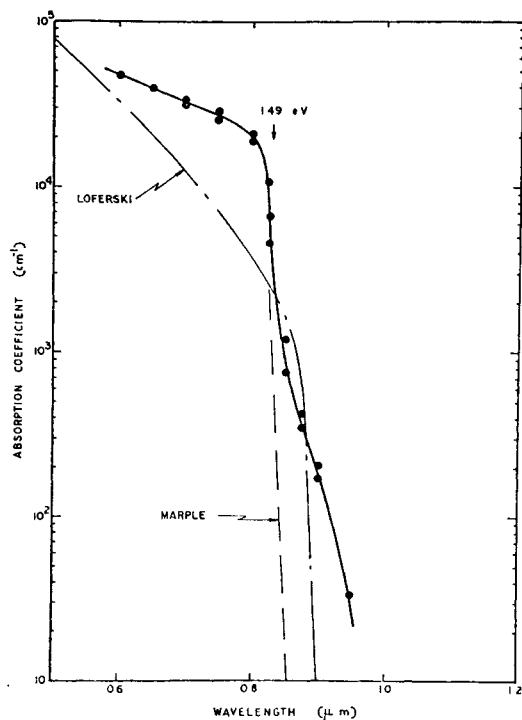


FIG. 3. — Optical absorption properties of CdTe. ● are experimental results on vacuum evaporated cubic thin films from unpublished work by Bell, Serreze and Wald. Loferski is from : Proceedings of the 10th IEEE Photovoltaic Specialists Conference, Palo Alto, 1973. Marple is from : *Phys. Rev.* **150** (1966) 728.

shows that the efficiency advantage of a higher bandgap compound is not nearly as great if recombination limited diodes have to be employed. This fact, of course, arises because large bandgap compounds transmit more of the IR energy of the solar spectrum and thus do not produce as high currents when compared with lower bandgap compounds. On the other hand, they utilize more fully the higher energy content of shorter wavelength photons to produce higher voltages. If, of course, recombination currents cause large nonidealities in the diodes employed, this advantage is quickly lost and it appears that this is where previously CdTe solar cells have fundamentally failed, a point to be explored somewhat further in the next section of this paper.

In the absence of an efficiency advantage over Si solar cells then, only the advantage of thin film fabrication remains. Such a cost advantage is tenuous though, because it depends very much on raw materials costs, minimum thicknesses that can be achieved, low cost substrates and so on. Some of these will also be explored in a later section of this paper. Nevertheless, these latter advantages are much more

unpredictable and a clear experimental verification of the efficiency predictions of Loferski using even small area but perfect CdTe single crystal solar cells would be, therefore, highly desirable. CdTe solar cells are also the subject of a separate review by M. Rodot in a later paper in this volume and various points only touched upon here will be discussed in detail there.

**2.7 NUCLEAR DETECTORS.** — Little needs to be said here about the potential of CdTe as a nuclear detector material because this constitutes the most promising application to date.

The combination of high average atomic number, high bandgap and reasonable mobility-lifetime products for both electrons and holes give CdTe a quite unique combination of properties for the purpose. Since most work in the area is also quite recent, I will not attempt any recapitulation here (Table IV).

TABLE IV

*Requirements for high resolution  $\gamma$ -ray detectors  
(based on Mayer [66] p. 462)*

Parameters	Requirements
1. Atomic number	$Z > 40$
2. Detector thickness	$d > 2 \text{ mm}$
3. Energy gap	$E_g < 1 \text{ eV (*)}$
4. Trapping centers	$N_T < 10^{14}/\text{cm}^3 (**)$
5. Carrier mobility (holes, electrons)	$\mu > 100 \text{ cm}^2/\text{V-s}$
6. Net carrier concentration	$ N_D - N_A  \leq 4 \times 10^{11}/\text{cm}^3$
7. Contacts	Noninjecting

(\*) For operation at room temperature and above, the effect of thermal excitation of intrinsic carriers must be considered, and there  $E_g > 1 \text{ eV}$ .

(\*\*) Assuming a cross-section of  $10^{-15} \text{ cm}^2$ .

Interestingly enough, when I tried to trace the history of CdTe for  $\gamma$ -ray spectrometry, I did find that the desirability of CdTe and other high  $z$  compounds apparently was recognized quite early by some people at Mobil Oil Co. which in 1961, filed a *prophetic* patent [62] explaining in some detail the advantages of high  $z$  compounds for  $\gamma$ -ray spectrometers when used in oil-bore-hole analysis, and CdTe was specifically mentioned as one of the desirable choices. However, nothing practical resulted according to one of the inventors [63] because the material was not readily available.

In 1966, however, Arkadeva *et al.* [64] published a paper on the subject and shortly thereafter the first paper by Mayer [65] appeared which marks the beginning of the continuing work at Hughes Research Labs. The subject is also treated in detail in the well known review paper by Mayer [66] and, of course, in the proceedings of the first Strasbourg Conference on CdTe [67].

As a final note to this short section, let me point out though that CdTe might also be usefully employed for the fabrication of highly sensitive avalanching detectors. However, it appears that this application has never been tried.

**2.8 THIN FILM STRUCTURES.** — A number of the previously described properties and effects have in fact been proposed for use in conjunction with thin film structures. Many of these structures are *hetero-junctions* and thus the listing below can only be viewed as a selection, because no exhaustive search on hetero-devices containing CdTe as one partner was conducted. One may, however, distinguish two groups of devices; the first of which uses high resistivity CdTe films, mainly in a supporting role or in some rather unique way.

Illustrative for this group are the applications reported by Bakirov *et al.* [68] and Yoshida *et al.* [69] (Fig. 5). The latter one is certainly an interesting application with considerable market potential. More unique uses are reported in refs. [70] and [71].

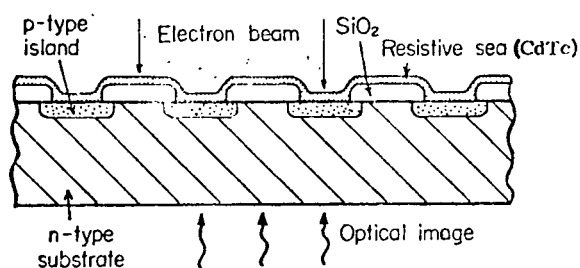


FIG. 5. — Schematic of a silicon vidicon target. From Yoshida *et al.* (Ref. [52]).

In the second group of more active devices we find an investigation of thin film triodes by J. Reynaud *et al.* [72] which appears quite interesting and the use of CdTe as a non-linear load impedance in integrated circuits [73].

Recently, CdTe has also been employed in conjunction with CdS in a *Matrix Photoelectric Image Converter* [74] and similarly in *Thin Film Photodiode Matrices* [75]. Finally in 1975 a novel charge storage diode structure again based on n-CdS-p-CdTe has been described [76], unfortunately, with little reference to the properties of the CdTe used (Fig. 6).

It is perhaps quite hard to ascertain why these applications are not in wide use, and they indeed may be, since manufacturers of the devices might not necessarily advertise the use of such components in their systems for competitive reasons.

More likely, though, it is still the somewhat unpredictable nature of CdTe thin films which prevents widespread use [72].

**2.8.1 Miscellaneous uses.** — A variety of miscellaneous uses has been reported for CdTe. In part these comprise electronic components which do not

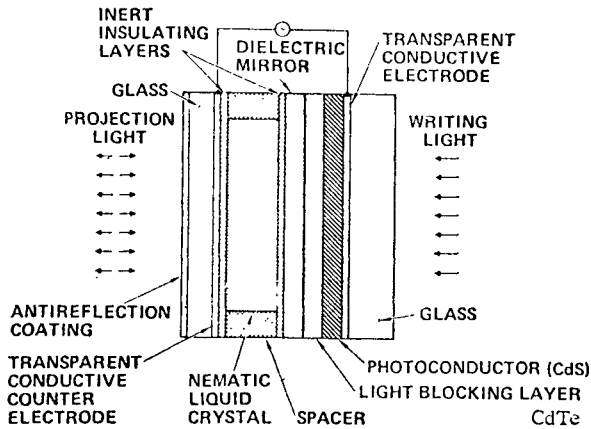


FIG. 6. — Schematic diagram of the a. c. photoactivated light valve used for projection display. From Fraas *et al.* (Ref. [76]).

it is easily sublimed and, therefore, thin film device processing should lead to definite fabrication advantages. Finally, as is pointed out below, the starting materials (Cd and Te) in semiconductor purity are quite competitively priced when compared to other semiconductors. Hence, all the conditions for widespread uses are fulfilled. Nevertheless, CdTe is not widely used in semiconductor electronics today.

This author believes that there are three definite and yet unresolved technical problem areas which need solution in order to make widespread application possible. These are discussed in the following.

**3.1 THE MINORITY CARRIER/« KILLER » CENTER PROBLEM.** — Even though the behaviour of both types of majority carriers in CdTe received detailed attention fairly early on, no comparable effort has been made to understand the behavior of minority carriers in CdTe as a function of doping and heat treatment, except in the high resistivity material used for  $\gamma$ -ray detection. This is somewhat surprising, since most of the applications potential of CdTe is in areas where minority carrier behavior is of the greatest importance.

Thus, to this day, there appears to be no consensus as to whether the 1.34 eV type of emission (Fig. 2) observed in all CdTe-based luminescent devices is in fact caused by recombination into just a simple Cd vacancy or into a donor-vacancy nearest neighbor associate according to the Williams and Prener model [82]. Equally, there are only very few rough estimates of minority carrier lifetime [83] and some cursory studies of drift length [84-86]. Neither of these two important parameters has been investigated systematically as a function of dopant type, concentration, heat treatment and stoichiometry.

In general, the fundamental pair lifetime has been assumed to be very short. But it does not have to be. That can be shown theoretically by using the models of van Rosebroeck and Shockley [87] and when this was done, employing the formulation presented by Bube [88] it could be shown [89] that even when doped to relatively low resistivity ( $10^{18}$  carriers/cm<sup>3</sup>), lifetimes  $> 10 \mu s$  should be achievable in CdTe. Experimental verification of such a contention can be found by considering the  $\gamma$ -ray detector materials. Here electron and hole lifetimes of  $\sim 1 \mu s$  are measured even though there are a variety of compensating donor and acceptor centers present in concentrations of  $\sim 10^{16}$  cm<sup>-3</sup> [86] (Fig. 8). However, the concentration of midgap centers in such materials is quite low. This brings us to another aspect of the problem which is best illustrated by making reference to one figure from the paper by Morehead [38] (Fig. 9) and noting that in all studies of electroluminescence a very large decrease in luminescent efficiency between 77 K-300 K was seen. This phenomenon has generally been attributed to *killer* centers near the middle of the bandgap.

fall in any of the coherent groups on which I have reported above such as Refs. [77] and [78] (Fig. 7). On the other hand CdTe has been employed in more esoteric uses such as in catalysis [79, 80] and in the

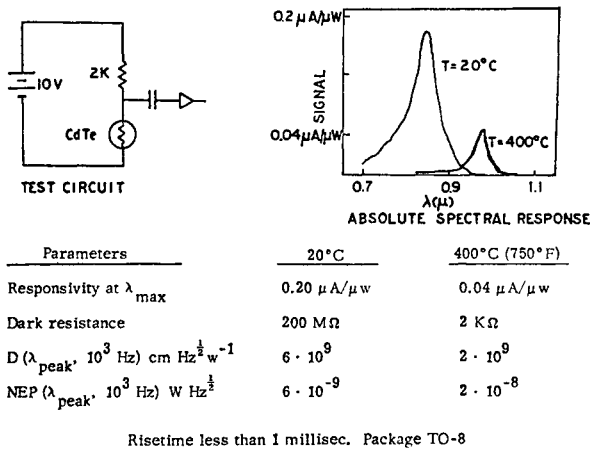


FIG. 7. — Operating characteristics for a CdTe high temperature photodetector. Farrell *et al.* (Ref. [78]).

photodecomposition of water [81]. The latter application is certainly worth pursuing somewhat further as an alternative to photovoltaics in solar energy conversion.

There may also well be other uses which have not been discovered in searches undertaken when this paper was prepared and since completeness in a paper such as the present one appears virtually impossible, I wish to again sincerely apologize to all those inventors who have been forgotten in the foregoing.

**3. Specific technical problem areas.** — As we have seen above, CdTe has significant application potential. Firstly, it does possess a number of useful physical properties which have applications in several areas of solid state electronics and optoelectronics. Also



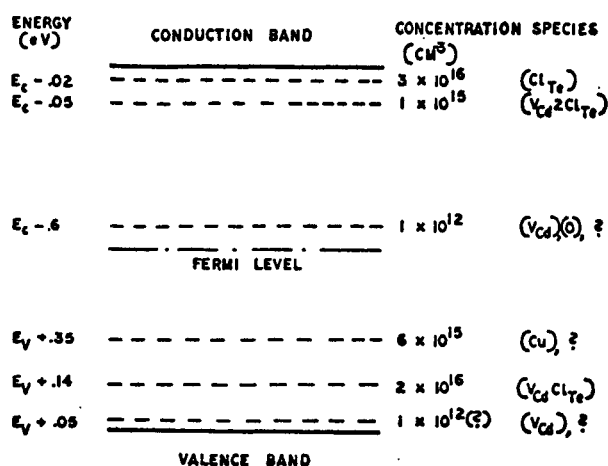


FIG. 8. — Energy level diagram showing the position of the energy levels, the concentrations, and the probable chemical origin of levels for Cl-doped CdTe. These levels were determined from measurements made on high resistivity, gamma-ray detector grade CdTe (Ref. [86]).

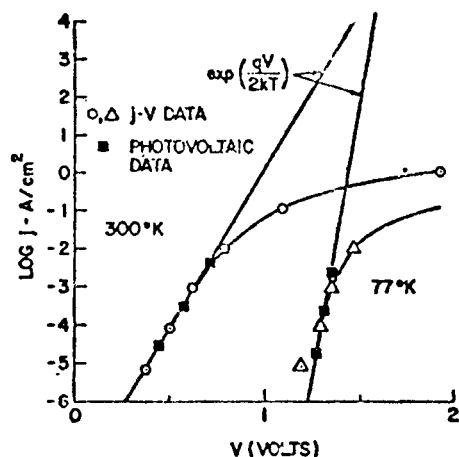


FIG. 9. — The current voltage ( $j$ - $V$ ) data for diffused diodes in CdTe. The logarithm of the current density  $j$  is plotted against the applied voltage  $V$ . The solid points are plots of the logarithms of the measured photovoltaic short-circuit current against the measured open-circuit voltage at several levels of illumination. From Morehead (Ref. [38]).

Equally, solar cells have always had unduly low open circuit voltages and, perusing the figure again, one reasonably can make the same centers responsible for this, since the large increase in  $V_{oc}$  at 77 K is quite obvious.

Since these are two significant applications for which CdTe holds high promise, it is surprising how little work has gone into trying to identify definitely the chemical nature of the responsible center. Naumov [90] already in 1966 reported emissions at 0.85 eV from Br and I doped CdTe, thus showing that radiative transitions occur at mid-gap. But only recently it appears have Gu *et al.* [43] tried to derive some information on the physical properties of the mid-gap centers in EL-diodes. Table V is taken

Table V

Average effective majority carrier concentration  $N_e$ , and width  $d$  of CdTe p-n junctions, and energy  $\Delta E_p$  and concentration  $N_i$  of deep centers in the p-type region of the junctions [43].

Diode No.	$N_e$ cm <sup>-3</sup>	$d$ nm	$E_p$ eV	$N_i$ cm <sup>-3</sup>
9	$6.6 \times 10^{16}$	142	0.68	$1.4 \times 10^{16}$
10	$1.7 \times 10^{17}$	89	0.67	$2.6 \times 10^{16}$
12	$8.5 \times 10^{16}$	125	0.68	$3.3 \times 10^{15}$

from their work and clearly shows the very significant concentration of centers at  $E_v + 0.68$  eV. They note that the origin of that center is unknown.

What then could these levels be? Firstly, one might suspect the  $V''_{C6}$ , situated at

$$E_v + (0.8-0.9 \text{ eV}) [91].$$

Since Gu *et al.* note that their activation energy measurements might be somewhat in error, this is quite possible. Also in Cl or In compensated material the number of such vacancies has been made quite small by association, thus the assumption is compatible with the results on  $\gamma$ -ray detectors.

Nevertheless, I feel that another possibility also deserves consideration. This is based on recent findings of the recombination behavior of Ge-doped CdTe by Nikonyuk *et al.* [92-94]. They found that Ge introduces two recombination states into CdTe, a fast one and a slow one, the depth of the slow one determined as  $E_v + 0.60-0.65$  eV.

Also, we have found [95] in investigations on Sn doped CdTe that even small traces of that element completely kill the transport of both carriers in high resistivity material ( $\mu\tau_e$  and  $\mu\tau_h < 10^{-7}$  cm<sup>2</sup> V<sup>-1</sup>). Such results on two neighbors of Si would have most chemists speculate on the properties of Si, which is an ever-present impurity in CdTe. If it were reasonably soluble and had properties similar to those of its neighbors, it could certainly be responsible for killer action in CdTe. It would thus seem useful to examine the role of Si in CdTe further.

In any event, it is clear that center gap killer centers in low resistivity n-type and p-type material must be more closely investigated, since their control would significantly enhance the practical utility of CdTe. In fact it appears that removal of such centers would greatly increase the lifetimes in both n- and p-type CdTe and thus would presumably allow preparation of far more efficient solar cells as well as room temperature EL diodes which could approach the  $> 10\%$  external quantum efficiencies so far only achieved under cooled conditions.

3.2 THE THIN FILM PROBLEM. — Although CdTe is quite easily prepared by sublimation, the thin film problem presents itself as the fact that only high

resistivity films are frequently obtained and control of film properties is quite difficult.

More specifically, the following observations may be noted :

a) Reasonable control over the majority carrier properties is possible only for n-type material and only for a limited number of deposition methods (close spaced vapor transport and vapor reaction sublimation in gas streams among them).

b) Good p-type material with low resistivity cannot be prepared by any thin film deposition method.

c) CdTe homojunctions cannot be prepared by thin film techniques.

d) Exceedingly short minority carrier lifetimes in both n- and p-type films, single and polycrystalline, are the rule and no detailed investigation of minority carrier behavior in thin films as a function of preparation conditions has been carried out.

These points have been described in a general way already by Cusano [96] in his 1967 review.

Although originally there were several hypotheses which involved only the presence of crystallographic line or volume defects to explain the high resistivities and anomalous photovoltage obtained [97, 98], further investigations demonstrated that there must be a significant influence of point defects, and Cd or Te vacancies or complexes involving these were invoked to explain the effects [98] (Fig. 10). There are still

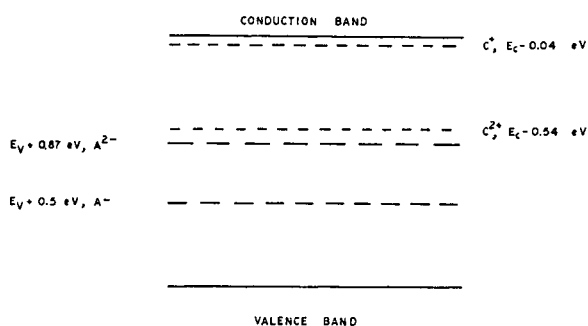


FIG. 10. — Trapping levels in evaporated CdTe films, after Kireev *et al.* (Ref. [99]). (C denotes a cation defect, A an anion defect.)

some problems with the details of all these explanations [100] and particularly the role of oxygen [101] and of grain boundaries [102] has been evaluated only in a preliminary way.

Also, some observations require the presence of two different defects for their explanation [103] and the presence of large numbers of two kinds of defects has recently been assumed in a new model in which the high resistivity in CdTe films is explained by postulating that the trap dominated lifetime in CdTe is shorter than the dielectric relaxation time of the semiconductor as it is in amorphous materials [104] (*relaxation semiconductor behavior*).

Of course, as I have pointed out, high resistivity films are often quite useful and may in fact represent a major practical use of CdTe. I equally feel, however, that the ease of sublimation is the major fabrication advantage of CdTe over other compounds and unless it can be employed for a variety of devices, very large scale use of the compound is not likely. In particular, use for terrestrial solar cells will be quite out of the question.

At present, it appears that line and volume defect problems may be overcome at least in single crystal films by proper preparation. In fact in his recent excellent review, Holt [105] stated that we are now at a point where single crystal films may be reproducibly prepared with a minimum of line or volume crystal defects.

Also, in the previous solar cell work by both Cusano [60] and Lebrun [61] it was shown that (at least for n-type) polycrystalline films with suitable concentrations and mobilities for majority carriers could be achieved. Thus, inhibition of majority carrier flow by extremely low mobility in the grain boundaries [102] can be avoided, but the short lifetime of minority holes in n-type material and the inability to prepare good p-type CdTe still represent significant problems which must be addressed with particular reference to the constraints of thin film deposition, before the technologist can make any realistic choice as to whether thin film CdTe can be advantageously employed for device fabrication and what methods are available to him.

Summarizing then, the ability to prepare thin films of CdTe by simple sublimation methods would give the compound a striking production advantage if indeed reliable fabrication of bi-polar structures with good control over minority and majority carrier behavior could be achieved. If in fact we are now in the position of having most of the crystallographic problems resolved so that good single crystal films can be prepared, a coherent effort to investigate all relevant electrical transport properties as a function of preparation and structure of the films is important, so that the various classes of CdTe devices can derive the true benefit from the significant advantages of thin film fabrication.

**3.3 THE CONTACT PROBLEM.** — The contact problem is one of long standing, already remarked upon by Kroeger and de Nobel in 1954 [11].

It is also hard to discuss because the definition of an *ohmic* contact in practice is a flexible one. Any contact which does not significantly perturb the characteristics of the desired devices in their range of operating temperatures is acceptable whether strictly ohmic in the physical sense or not. These practical principles of providing contacts to wide bandgap II-VI compounds have been described in some detail by Aven and Swank [106] from which the above definition has been adapted.

They also note the two main principles by which contacting may be achieved :

a) Establish a proper work-function match on the surface so that the contact may provide a sufficient carrier supply under all conditions of operation.

b) Lower the surface barrier and cause it to be as thin as possible by heavily doping the region underlying the contact to provide a high tunneling probability for carriers from the semiconductor to avoid rectification.

In both cases one has to start by knowing the nature of the semiconductor surface which determines its electron emission behavior (work-function).

On the most fundamental level, this involves a consideration of surface bonding which leads to the concept of *surface states* which in turn determine the behavior of the metal semiconductor barrier [107, 108].

In this scheme, then CdTe appears as a special case of a covalent, surface state dominated material [109].

The fundamental surface properties of CdTe relevant to contacting have been evaluated in the classical paper by Swank [110] (Table VI). His deter-

TABLE VI

*Surface parameters of n-type CdTe, high vacuum cleaved on the (110) plane (after Swank) [110] in electron volts*

Electron affinity $\chi$	Work function $\phi$	Band bending	
		$eV_D$	$eV_{SPV}$
4.28	4.67	0.23	0.29
Electron affinity plus bandgap 5.78	$\phi$ gold on CdTe 5.08	$\chi - \phi$ Au 0.80	$\Delta\phi$ Measured 0.63

mination of an electron affinity of 4.28 eV on n-type (110) CdTe cleavage surfaces in ultrahigh vacuum has recently been discussed by Marks [111] in terms of a theoretical model. The acceptor like surface state implicit in the results of Swank is interpreted as resulting from mixed binding when all Cd atoms in the surface are rotated up or the Te atoms are rotated down. Thus, the theoretical model and the experiments are consistent for this case.

However, one immediate difficulty which arises is the fact that the polar surfaces, such as (111) (consisting only of Cd or Te atoms respectively) are not accessible for these experiments, since they do not cleave. Given the results cited above, however, one might suspect that such surfaces have significantly different properties which are yet to be explored.

The true surface state, obtained under high vacuum conditions will also be immediately modified by absorption (chemisorption) when exposed to real

atmospheres. Undoubtedly, this effect is significant for CdTe [101]. Lebrun [61] for instance demonstrated that a freshly vacuum evaporated film of n-type CdTe when contacted immediately with  $Cu_{2-x}Te$  formed a barrier which increased appreciably when exposed to air and even more when exposed to ozone (Fig. 11). Also the generally noted absence of

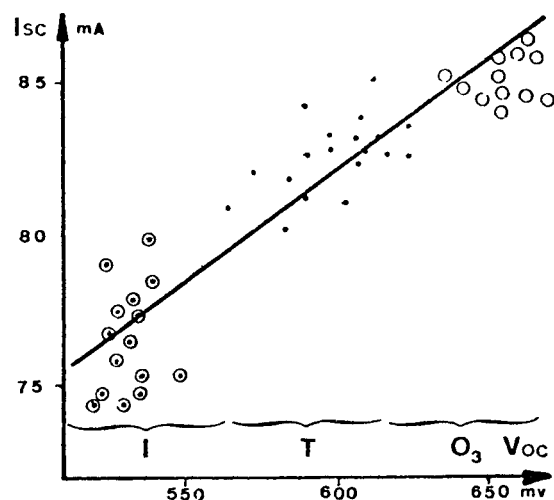


FIG. 11. — Barrier height of a CdTe- $Cu_{2-x}Te$  photovoltaic junction as a function of oxygen chemisorption. From Lebrun (Ref. [61]). (For details see text of referenced paper).

surface leakage on arbitrarily prepared and unprotected CdTe  $\gamma$ -ray detectors is perhaps best explained by passivation via chemisorption of some species common to most laboratory atmospheres.

Since oxygen is not easily desorbed even under vacuum [101], one might suspect that noble metals such as Au and Pt could show barrier behavior on this basis alone, whereas metals such as Al or perhaps even In which can reduce the oxygen at the surface, might be expected to more clearly reveal the behavior of the CdTe surface itself. Of course, other chemisorbed species such as water [101] must also be considered in this context.

Since etching and heat treatments are also often employed before or during contact formation, further complications have to be considered. Among these are the loss of Cd from the surface and a consequent inversion of an n-type surface [112] into p-type, for instance when heated in vacuum or inert atmosphere. However, when oxygen is present during heating, preferential oxidation of the Cd to CdO can occur on the surface. In this way, n-p-p structures on p-type material and n-p-n structures on n-type are formed [113] (Fig. 12). Hence the curious fact that one can sometimes obtain rectification with all metals on both types of material can be explained. Finally, etching and subsequent rinsing can cause hydrolysis of Te ions and thus results in the deposition of Te on the surface [114], again falsifying results based on clean surface behavior.

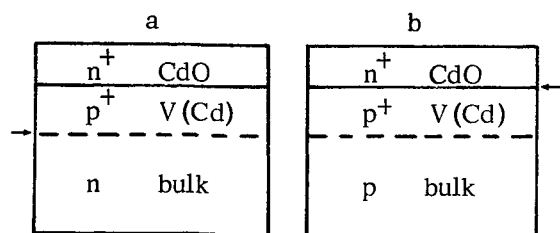


FIG. 12. — Model of the surface of n-type (a) and p-type (b) cadmium telluride crystals. Here,  $n^+$  represents a semiconductor layer formed as a result of oxidation of the surface, and  $p^+$  represents a layer formed as a result of loss of cadmium atoms at the surface. From Akobirova *et al.* (Ref. [113]).

All these surface and sub-surface effects are undoubtedly responsible for a great deal of the confusion which now exists regarding contacts to CdTe. They also can account for the great popularity of the electroless deposition techniques which were employed early on [11]. Furthermore they help explain why it is generally necessary to use various *drive in* treatments such as arcing [11] to obtain good contacts to n-type material even with low work-function metals such as Al and In.

Nevertheless, these effects, once understood and taken seriously can be controlled, although a systematic and determined effort may be necessary to accomplish this goal which also depends very much on the details of the device to be contacted and the fabrication procedure to be used.

Even after resolving all these cumbersome and distracting (although important!) side issues, one may still expect to encounter the fundamental problem for highly doped p-type materials, namely that the valence band edge is situated 5.78 eV below the vacuum level [110] and thus for material which is heavily doped with shallow acceptors, no match with a suitable work-function metal is available to produce a good ohmic contact. Also, very high concentrations of p-type dopants are hard to introduce, thus tunneling, contacts will not be easy to prepare although under the proper conditions phosphorous perhaps could be used successfully [115].

Of major importance then is the nature of the barrier produced by the various electroless metal contacts, since in any case one would like to make it as low as possible.

One reason for the popularity of such electroless contacts, as pointed out above, is obviously the fact that the electrochemical reaction proceeds significantly below the surface thus avoiding many of the cited surface complications.

Another reason may well be that an actual lowering of the barrier occurs, because it has been demonstrated recently that the electrochemical exchange does not generate pure metal on the surface but results in a mixture of Te and a metal-telluride [116, 117, 118]. In fact on the basis of the evidence reported,

we have suggested that [119] a rather straightforward electrochemical reaction occurs in the Pt case :



Also, mixtures of Te and small bandgap tellurides have been prepared by etching in a way especially designed to produce fresh Te layers on the surface into which subsequently metals such as, for instance, Ni are evaporated to form similar mixtures [120, 86] resulting in reasonably ohmic contacts to p-type materials.

Since Te [121] and many of the tellurides [121] which are generated by this method are degenerate semiconductors, one might envision a quasi-ohmic contact to be formed if the right relationships of the respective valence bands occurred (Fig. 13). It appears



FIG. 13. — Generalized band-scheme for contacting a larger bandgap compound with a smaller bandgap compound. (Possible potential spikes are neglected here.)

that such a contact is perhaps the only one available for highly doped p-type CdTe. It would thus be of great interest to form various small bandgap tellurides on clean p-type CdTe surfaces and evaluate the resulting contact behavior. Also Te needs to be further evaluated as a contact [122] and its possible utility assessed.

For devices which require very low contact resistances, such as solar cells, all this could cause a severe problem, and since it admits only of an extremely small range of solutions, it may well turn out to be the limiting problem for certain CdTe homojunction devices.

**4. Rudimentary materials economics.** — Current prices (May 1976) for high purity Te, Cd, Ga and As as quoted by one of the major suppliers are shown in table VII. As one can readily see, Cd and Te are quite competitively priced with respect to other semiconductors, so cost should be no barrier to the introduction of regular CdTe based electronic devices. Particularly in the very competitive area of electroluminescent diodes the raw materials cost advantage over GaAs could be significant. If thin film fabrication of the appropriate CdTe devices were to become possible, the cost advantage could be quite overwhelming. Also one can confidently state that in these kinds of applications in which the total amount of material used is small, no particular supply difficulties need to be expected.

However, in the case of large scale use of CdTe solar cells which are to generate significant amounts of bulk power, the situation becomes somewhat more involved than just comparing prices in table VII.

TABLE VII

Prices for various semiconductor grade materials  
(in quantities of 5 to 20 kg)

Te	99.999 9+ %	\$ 108/kg
Cd	99.999 9+ %	\$ 70/kg
Ga	99.999 9+ %	\$ 1 000/kg
(no quantity discounts)		
As	99.999 9+ %	\$ 410/kg
Te	Technical grade 99.5 %	~ \$ 13.20/kg
Poly-Si	Semiconductor	~ \$ 69/kg

It is now necessary to evaluate the total available supply of a rare element such as Te which is obtained only as a by-product in other mining and refining operations. This then allows an estimate of the technical goals (film thickness, efficiency) which must be achieved to make any reasonable impact on the supply of electrical power. Only after such an impact has been evaluated can more detailed economic analysis proceed.

Thus let us note two cases :

The amount of Te and Cd needed for a one Gigawatt (peak) electrical generating station :

- 1) 5 % efficiency, 10  $\mu$  CdTe thickness, 590 (metric) tons,
- 2) 10 % efficiency, 2  $\mu$  CdTe thickness, 59 (metric) tons.

We can now compare this against the total reserve of Te (which we will assume is limiting) from copper and lead ores in the U. S., which has been estimated as 3,268 tons [123]. This, for the first case would only give us 5.5 (peak) GW of electric power from indigenous U. S. Te resources, scarcely enough to make a difference, since the total installed electrical capacity in the U. S. in 1974 was 495 GW [124] and not more than a 20 % duty cycle can realistically be expected from a solar power plant, whereas the duty cycle for overall electric power generation was ~ 45 % [124]. The second case is more interesting but still somewhat marginal. It is clear on this basis alone that we must strive for very thin films and high efficiencies and perhaps for moderate concentration of sunlight for which CdTe, because of its high bandgap, should be ideally suited. Some work could also fruitfully be directed towards CdSe and CdTe CdSe solid solutions since Se is about 10 times as abundant as Te [125].

Perhaps also, the estimate of a *total* reserve of 3,268 tons from copper and lead ores in the U. S. is somewhat low because the recovery ratios are variable and have been as low as 5 % only [125]. Also, this estimate was made in 1965 and ever since, the U. S. has had an annual Te production of ~ 180 tons (metric). Hence the estimate would imply that the U. S. will run out of copper and lead ores in less

than 10 years which is not borne out by other estimates. On the other hand, not all of the copper slimes from which Te was produced in the U. S. originated from U. S. derived ores. Taking all these somewhat contrary factors together, I would estimate that ~ 10 X as much of a *total* reserve exists. However, I am not a mineralogist at all and thus the only contribution made by this paragraph is the demonstration that total Te availability is very hard to estimate on the basis of simple mineralogical facts.

It is, of course, also necessary to point out that countries other than the U. S. might be blessed with a better ratio of available Te to overall electric power consumption and thus the incentive to develop CdTe solar cells could be much greater.

Finally, reference must also be made to the question of Te recovery from minerals other than those which contain Cu and Pb which, according to the excellent survey of Sindeeva [126], is not at all unreasonable to expect. It appears then that more mineralogical/metallurgical work is urgently needed in estimating Te recovery and economics from all reserves. This is, however, a very basic economic study which I believe is not presently amenable even to fruitful speculation.

One final note should perhaps be that *all* the available Te could likely be used for a purpose such as solar cells since it has apparently no use in which it cannot be relatively easily replaced by either sulfur or selenium [125].

**5. Conclusions.** — CdTe is a quite well behaved semiconductor material. It can be doped p- and n-type and both carriers possess reasonably good mobilities.

Its bandgap of 1.5 eV lies in an interesting intermediate range and can be relatively easily changed by alloying. It displays a number of physical effects which in combination could have utility in various semiconductor components, particularly in optoelectronics. Furthermore, its components (Cd and Te) are relatively inexpensive, even though they are rare by-product metals, because they can be easily refined to semiconductor purity.

Finally, the compound can be readily obtained in thin film form, which should give it a definite fabrication advantage in many applications. Hence, this review has shown that many applications have been proposed and carried through the laboratory stage and in all but one group (Gunn effect devices !) CdTe seems to possess fundamental technical and/or fabrication advantages over competitive semiconductors which one might choose.

The reason why it is not more widely employed is found in the fact that the compound seems to forever fall short of achieving its fundamental potential.

There appear to be three major reasons for this :

- 1) The minority carrier behavior as a function

of preparation and doping is poorly understood and cannot be controlled.

2) Thin film technology leads to quite erratic products in which neither majority carrier nor minority carrier behavior are clearly understood or can be reproducibly controlled.

3) Contact technology is poorly developed and may be limited in low resistivity p-type material to a very small number of possible choices.

Resolution of the first problem is essential because most of the practical interest for CdTe revolves around optoelectronic/minority carrier devices (EL-diodes, solar cells,  $\gamma$ -ray detectors, photo-diodes [arrays-charge coupled devices]), and even in laser windows and electro-optic modulators trapped charges

can be a nuisance if the centers are not precisely known.

Realistically speaking, however, many of these applications would become interesting (against already well entrenched competition from better known semiconductors with a larger technology base) only if the striking advantage of cheap thin film fabrication could be demonstrated to be reproducibly possible.

Finally, the contact/barrier questions now existing need to be clarified since in some classes of devices (such as solar cells) they could be the limiting factor to the realization of simple homojunction devices, and even in  $\gamma$ -ray detectors they appear to be one factor which causes a lot of trouble in the application of the devices.

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