THERMAL PROPERTY MEASUREMENT TECHNIQUES
AND SOME RESULTS FOR CdTe
AND (Hg,Cd)Te ALLOYS

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FINAL TECHNICAL REPORT FOR THE PERIOD
MARCH 10, 1983 TO FEBRUARY 29, 1984

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In order to improve the manufacturing techniques for semiconductor materials
as well as establishing the operating performance characteristics, the
thermophysical properties, thermal conductivity, specific heat, expansion
coefficient, emissivity and heat of fusion are required. Some of these
properties have been measured for CdTe and (Hg,Cd)Te. In addition to these
results, measurement techniques are also described.
SUMMARY

The objective of this program is to develop techniques for the measurement of thermophysical properties of semiconductor materials (GaAs, CdTe, HgTe, and (HgCd)Te alloys). The specific properties of interest are thermal conductivity (room temperature to 500°C), specific heat (room temperature to 250°C), thermal expansion coefficient (room temperature to 500°C), and the heat of fusion. Higher and lower temperature range measurements are also to be considered.

The research and development approach being used in this program is to, 1) utilize existing measurement equipment at Geoscience to obtain as many of the outlined properties as possible, 2) make equipment modifications and improvements to increase the temperature range for the measurements as permitted by the budget and 3) evaluate the experimental data obtained on the basis of the physical mechanisms that characterize semiconductor materials.

The accomplishments during the current contract period* are as follows:

1. Thermal conductivity, specific heat, thermal expansion coefficient and gray body emissivity measurements were made for the semiconductor CdTe at specific temperature levels.

*The program consists of a total 700 manhour effort.
2. Thermal conductivity and thermal expansion coefficient measurements were made for the semiconductor alloys (HgCd)Te for specific temperature ranges.

3. A high-temperature gradient layer type calorimeter that can operate up to 800°C was designed, fabricated and checked out.
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I. INTRODUCTION

In order to improve the manufacturing techniques for semiconductor materials as well as establishing their operating performance characteristics, further information on the thermophysical properties is required. Typical materials of interest are mercury telluride, cadmium telluride, mercury/cadmium telluride alloys and gallium arsenide. The primary thermal properties of interest are the thermal conductivity, specific heat, expansion coefficient, emissivity and the heat of fusion.

Geoscience's responsibility is to make these measurements over a range of temperature conditions and for specimen sizes that are currently available. This report outlines the measurement techniques used, the results obtained to date, some of the difficulties being encountered and discusses the results and future measurement work.
II. THERMAL PROPERTY MEASUREMENT TECHNIQUES

The measurement methods that are being used in this program are described briefly in the following paragraphs.

A. Thermal Conductivity

One method that is used to measure the thermal conductivities of crystalline materials is the axial heat flow or comparative method as it is sometimes called. Figure 1 shows the elements of the technique. Heat flows from a heat source (a resistance heater) through thermal conductivity standards positioned on both sides of a test sample. These elements consist of short cylinders. The heat is removed from the other end of this composite rod by a cooling system. There are also guard heater windings around the composite rod to minimize radial surface heat losses. The outer structure of the system consists of annular insulation. Thermocouples are positioned axially along the composite rod as shown in the figure. The system may or may not be located in a vacuum environment. A classical heat balance at steady state involving known measured temperature gradients and thermal conductivities of the standard materials makes it possible to determine the thermal conductivity of the test sample.

A second method for measuring the thermal conductivities of crystalline materials is the guarded hot plate or twin-plate method.
Figure 1. Rod heat conduction (comparative) thermal conductivity system.
Figure 2 illustrates the major elements of the system. Heat from a central, flat plate heater flows through two hot plates, through two test slabs to two cooling plates. The temperature differences across the two test samples are determined from thermocouples that are embedded in the hot and cold plates or in the test samples. As shown in the figure, the central heater is surrounded by a guard heater. A thermopile is positioned between the central hot plates and the guard hot plates. At steady state, when the central heater and guard heater have been adjusted so that the thermopile output is very small (yielding unidirectional heat flow), a data set is obtained. From a heat balance on the system involving heater power inputs, heat transfer areas, temperature differences and sample thicknesses, the thermal conductivity can be determined. Figure 3 shows a photograph of a typical guarded hot plate measurement system in use at Geoscience.

B. Specific Heat

One convenient way of measuring the specific heat of crystalline materials is by utilizing a gradient layer calorimeter. The elements of such a system are shown in Figure 4. A test sample is positioned inside of the heat flux measuring envelope that is housed in a fluid cooled heat sink. The heat sink in turn is surrounded by thermal insulation. Figure 5 shows a photograph of an assembled gradient layer calorimeter.

This calorimeter is based on the principle that all of the heat flow
Figure 2. Guarded Hot Plate (Twin Plate) Thermal Conductivity System.
Figure 3. Guarded hot plate thermal conductivity apparatus (disassembled view).
Figure 4. Elements of a Gradient Layer Calorimeter System.
Figure 5. Photograph of an assembled gradient layer calorimeter.
into or out of the calorimeter must pass through its walls where
the temperature gradient sensors are located. Therefore, the calori-
meter envelope integrates the total heat flow in the system on an
instantaneous basis. The calorimeter walls consist of special thermo-
electric heat flux transducers* that yield a DC voltage output signal.
The calorimeter walls are thin so that low time constants are in-
volved. As heat flows through the walls, a small temperature dif-
ference directly proportional to the heat flow is developed. In a
properly designed calorimeter, the output signal is affected only
by the rate of heat flow.

The utilization of the calorimeter to measure the specific heat of
a material is done as follows: An unloaded calorimeter that has
come to thermal equilibrium at temperature level $t_1$ is suddenly ex-
posed to a new temperature level, $t_2$. The heat flow trace as the
transient process proceeds from the initial steady state condition
to the final steady state condition can be obtained with a recording
potentiometer. The area under this curve is equal to the heat added
to or extracted from the calorimeter and its liner for the superposed
temperature perturbation. Next, the calorimeter is loaded with the
specimen to be investigated and again exposed to the original tem-
perature $t_1$ and allowed to equilibrate. Then the loaded calorimeter
is suddenly exposed to the new temperature datum $t_2$, allowed to reach

*A heat flux transducer is composed of a thermopile system that
has "hot" junction sets at one depth within the sensor and "cold"
junction sets at another depth.
equilibrium and the corresponding transient heat flow trace recorded. The area under this curve is equal to the heat added to or given up by the calorimeter, its liner and the specimen. Subtraction of the areas under the two transient traces yields the desired heat flow for the specimen alone. The trace area is related to an energy flow per unit time by means of an accurate resistance heating calibration for the calorimeter. The heat capacity for the specimen is obtained from the classical definition (heat transferred divided by the product of the mass and temperature perturbation). The defining equation for the specific heat, $c_p$, is

$$c_p = \frac{\int_0^{\theta_e} \left( q(\theta) - q(\theta)_e \right) d\theta}{m_s \left( t_2 - t_1 \right)}$$

where:

- $q(\theta)$, time dependent heat flow through calorimeter when loaded with test sample
- $q(\theta)_e$, time dependent heat flow through calorimeter without the test sample
- $\theta$, time
- $\theta_e$, the equilibrium time period (no further heat flow)

$m_s$, mass of the test sample

$t_1$, initial temperature datum

$t_2$, final temperature datum
C. Thermal Expansion Coefficient

The thermal coefficient of expansion for materials is normally measured by the classical dilatometer method. Specifically, the differential length change between a test rod of the material being investigated and a low expansion coefficient standard rod or tube (such as a quartz) is measured. Figure 6 illustrates the most common arrangement. The system is surrounded by a constant temperature furnace that allows the temperature datum to be controlled. The relative expansion between the test specimen and the quartz is measured with an accurate, highly sensitive dial gauge. From the differential expansion measurement and the known expansion coefficient of the quartz, the expansion coefficient of the test material is determined.

D. Gray Body Emissivity

There are two methods that can be utilized to measure the gray body emissivity of semiconductor materials. One method requires the utilization of two test surfaces that are positioned between a central heater; this system, which is used in a hard vacuum environment was described in the first quarterly report (GLM-322). An alternate emissivity test method involves the utilization of a single test surface which need not be located in a hard vacuum. Specifically, a small plate of semiconductor material (containing a laterally drilled thermocouple hole to the center) is positioned on top of a calibrated heat flux sensor which is in turn located on a surface heater that
Figure 6. Thermal expansion coefficient (dilatometer) system.
generates the heat flux flowing through the system (see Figure 7).

The steady state heat loss from the surface of the semiconductor test sample is composed of natural convection to the surrounding air and thermal radiation to the surrounding environment. It is noted in Figure 7 that the environmental radiant temperature is in essence defined by a mean surface temperature of a horizontal panel spaced some distance above the test apparatus. The equation describing the energy exchange is,

\[ q_A = h_{cv} (t_s - t_a) + h_{rp} \epsilon (t_s - t_{mr}) \]  

(2)

where,

- \( q_A \) : total heat flux from test surface
- \( h_{cv} \) : natural convection conductance of surface
- \( t_s \) : surface temperature
- \( t_a \) : ambient air temperature
- \( h_{rp} \) : Planckian radiation conductance of surface (a known function of \( t_s \) and \( t_{mr} \))
- \( \epsilon \) : gray body emissivity
- \( t_{mr} \) : mean radiant temperature
Figure 7. Schematic diagram showing the single slab emissivity test system.
Although one can predict the convective conductance, $h_{cv}$, from fundamental natural convection theory, the accuracy is probably no better than about $10 - 15\%$ for the specific geometry involved; therefore, it is best to determine the convective conductance by experiment, as follows: First use a test sample that has a Planckian surface, (or one that has a known, high emissivity). Under these conditions, the convective heat loss can be determined by subtracting the known radiation heat loss for the Planckian surface and mean radiant temperatures involved from the total heat loss through the circuit (as determined by the heat flux sensor); thus, the convective conductance is established.

The measurement for a gray body emissivity of a semiconductor is next made. Specifically, the unknown sample is inserted in the apparatus shown in Figure 7 and all temperatures and the total heat flux are measured at equilibrium. Finally, these values and the conductances $h_{cv}$ and $h_{rp}$ are substituted into Equation 2, from which the gray body emissivity, $\varepsilon$, is obtained.
III. MECHANISMS THAT CONTROL THERMAL PROPERTIES

Some time has been spent on reviewing the theoretical thermal property expressions in the literature. Major emphasis has been given to the thermal conductivity.

In the case of heat conduction through semiconductors, the conductivity is generally given as the sum of lattice and electronics terms. Leibfried and Schlömann give an expression for the lattice component as a function of several constants and semiconductor material parameters, namely, the Boltzmann constant, Planck’s constant, the mass per atom, the volume per atom, the Debye temperature and the Grüneisen parameter (which is related to the thermal expansion coefficient). Casimir gives a function that relates the lattice conductivity to the specific heat, phonon velocity and the mean free path associated with boundary scattering. Keyes develops a lattice conductivity expression that contains a melting temperature. The electronic conductivity is shown by Drabble and Goldsmid to be dependent upon mobility and the number of change carriers. The electronic conduction terms for semiconductor is usually much smaller than the lattice conduction term in practical temperature ranges.

In the case of thermal expansion, Grüneison relates this quantity to the specific heat, the compressibility, the volume and the Debye temperature. It is also shown that the ratio of thermal expansion
coefficient to specific heat is not temperature dependent.

In the case of the specific heat, classical expressions derived from quantum theory concepts make it possible to define this property in terms of the molecular weight, the Boltzmann and Planck constants and the absolute temperature.

Crystal dislocation, impurities and heat treatment are parameters that affect some of the prediction functions in complicated ways.
IV. RESULTS

A major problem associated with issuing thermal property measurements for semiconductor crystal materials is that the test samples must be representative of materials to be used in focal plane measurement systems. Various growing methods are being used to date to produce semiconductor materials. Small differences in composition can thus occur that influence carrier concentrations. Crystal imperfections can also occur. Recrystallization and annealing processing can also affect the thermal properties. Therefore, thermal property measurements reported for a given material should be accompanied by a quantitative description of the sample preparation (material characterization).

In the current study period, property measurements were made for semiconductor materials supplied by Amorphous Materials, Inc., and by Texas Instruments, Inc. The characterization information supplied by these two organizations is given below:

CdTe (grown by Amorphous Materials, Inc.)

The plate samples supplied were grown in solution as described in Amorphous Material's Report No. 8 (October 1 - December 31, 1983). The plate weighed 3.3 Kgms and was 8 inches in diameter. The growth conditions cited in Table I were: Cd 42 Te 58, 1050, 3°C/hr.
(Hg,Cd)Te Alloy (grown by Texas Instruments, Inc.)

The rod samples (diameter = 6.3 mm and length = 25 mm) were described by their mole percentages. These materials were compounded at these percentages and then recrystallized in a mercury vapor atmosphere.

A. Thermal Property Measurements for CdTe

The measurements made to date for this semiconductor material are shown in Table I.

B. Thermal Property Measurements for (Hg,Cd)Te Alloys

The thermal property measurements made to date for these semiconductor materials are shown in Table II.

C. High Temperature Gradient Layer Calorimeter

A gradient layer calorimeter having the inside dimensions, 25 mm diameter by 76 mm long, was designed and fabricated for operation at higher temperatures than the one that was previously used at Geoscience to make the specific heat measurements for CdTe. This new calorimeter, shown in Figure 8 with a test capsule, can also be used to measure heats of fusion for materials whose melting temperatures can be as high as 800°C. The calorimeter is constructed of mullite and the thermoelectric materials are Chromel-Alumel.

The calorimeter is calibrated by placing a small electric heater inside the device; upon dividing the measured electric heat generated
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity</td>
<td>0.0095 cal/sec cm°C</td>
<td>$t_{\text{mean}} = 38°C$</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>0.061 cal/gm°C</td>
<td>$t_{\text{mean}} = 38°C$</td>
</tr>
<tr>
<td>Thermal Coefficient of Expansion</td>
<td>$1.96 \times 10^{-6}$ l/°C</td>
<td>$24°C &lt; t &lt; 210°C$</td>
</tr>
<tr>
<td>Gray Body Emissivity</td>
<td>0.79</td>
<td>$49°C &lt; t &lt; 210°C$</td>
</tr>
</tbody>
</table>

**TABLE I**

**THERMAL PROPERTIES MEASUREMENTS FOR CdTe**
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity of Hg$<em>{0.69}$Cd$</em>{0.31}$Te</td>
<td>0.0041 cal/sec cm°C</td>
<td>$t_{\text{mean}} = 81^\circ\text{C}$</td>
</tr>
<tr>
<td>Thermal Conductivity of Hg$<em>{0.796}$Cd$</em>{0.204}$Te</td>
<td>0.0048 cal/sec cm°C</td>
<td>$t_{\text{mean}} = 81^\circ\text{C}$</td>
</tr>
<tr>
<td>Thermal Coefficient of Expansion of Hg$<em>{0.796}$Cd$</em>{0.204}$Te</td>
<td>$2.86 \times 10^{-6}$ 1/°C</td>
<td>$24^\circ\text{C} &lt; t &lt; 93^\circ\text{C}$</td>
</tr>
<tr>
<td>Thermal Coefficient of Expansion of Hg$<em>{0.775}$Cd$</em>{0.225}$Te</td>
<td>$3.49 \times 10^{-6}$ 1/°C</td>
<td>$24^\circ\text{C} &lt; t &lt; 93^\circ\text{C}$</td>
</tr>
<tr>
<td>Thermal Coefficient of Expansion of Hg$<em>{0.69}$Cd$</em>{0.31}$Te</td>
<td>$3.22 \times 10^{-6}$ 1/°C</td>
<td>$24^\circ\text{C} &lt; t &lt; 93^\circ\text{C}$</td>
</tr>
</tbody>
</table>
Figure 8. Photograph of the high temperature calorimeter and a test capsule.
by the millivolt output signal of the calorimeter thermopile at steady state, the calibration constant for the device is established.

The high temperature calorimeter has been used to check the CdTe specific heat measurements made previously using Geoscience's normal temperature gradient layer calorimeter. The comparisons were good.

In preparation for the utilization of the gradient layer calorimeter to determine the heats of fusion of semiconductor materials, a series of measurements were made for the metal tin. Specifically, a sample of pure tin was inserted into Geoscience's normal temperature calorimeter and heat of fusion measurements performed (for both heating up and cooling down processes). The recorded output voltage results for the calorimeter heat flow and sample temperature as functions of time are shown in Figures 9 and 10. The general calorimetric equations from which the heat of fusion is obtained (illustrating and heating case) are expressed as follows. The total heat added to the calorimeter in raising the system temperature from a temperature below the fusion temperature to a new value that lies above the fusion temperature is composed of a number of terms, namely,

\[ \int_{0}^{\theta_e} q(\theta) \, d\theta = m_s \, c_p \, (t_2 - t_1) + m_L + m_s \, c_p \, (t_3 - t_2) + m_c \, c_p \, (t_3 - t_1) \]  

(3)

where:

- \( q(\theta) \), time dependent heat flow through calorimeter when loaded with test sample
FIGURE 9
Heat of Fusion Measurements With a Standard (Heating Case)
FIGURE 10
Heat of Fusion Measurements With a Standard (Cooling Case)
\[ q, \text{ time} \]
\[ t_e, \text{ equilibrium time period (no further heat flow)} \]
\[ m_s, \text{ mass of test sample} \]
\[ c_{p_s}, \text{ specific heat of test sample in solid state} \]
\[ t_1, \text{ initial temperature of system (below fusion value)} \]
\[ t_2, \text{ fusion temperature} \]
\[ L, \text{ latent heat of fusion} \]
\[ c_{p_L}, \text{ specific heat of test sample in liquid state} \]
\[ t_3, \text{ final temperature of system (above fusion value)} \]
\[ m_cp_c, \text{ product of mass and specific heat of calorimeter heat flux sensor and sample liner (determined from an empty calorimeter run)} \]

Rearrangement of Equation (3) yields,

\[
L = \frac{1}{m_s} \int_0^{t_e} q(\theta) \, d\theta - c_{p_s}(t_2 - t_1) - c_{p_L}(t_3 - t_2) - \frac{m_c}{m_s} c_p (t_3 - t_1) \tag{4}
\]

Note that the quantity \( q(\theta) \) is expressed in terms of the product of a calorimeter calibration constant, \( C \), and an output voltage, \( E(\theta) \),

\[
q(\theta) = C E(\theta) \tag{5}
\]

The heats of fusion for tin obtained for the heating and cooling runs shown in Figures 9 and 10 agreed within 6 percent.
V. DISCUSSION

During the March 10, 1983 - February 29, 1984 program period, some thermal property measurements for CdTe and (Hg,Cd)Te were made with existing equipment; also a higher temperature calorimeter was designed, fabricated and tested.

Some difficulties have been experienced in the program. One problem involves the procurement of representative test samples with complete material characterization. Another problem relates to the limited sample sizes available. A third problem in California involves handling and disposal of poisonous materials.

As more data sets are obtained by Geoscience, attempts will be made to interrelate some of the thermal properties being measured, using the theoretical property functions noted in this report.

The next year's study proposal for this program includes, 1) the modification of measurement systems to work with smaller samples, 2) the completion of one or more data sets and 3) the performance of lower temperature measurements.
VI. REFERENCES


