DOE/NV/ 11502--76

Final Technical Progress Report for:

"Mercuric Iodide Research and Development in Support of DOE Historically Black Colleges and University Program"

July 31, 1996

Prepared by: M. A. George, K.-T. Chen and A. Burger
Department of Physics, Fisk University, Nashville, TN 37208

Submitted to:

U.S. Department of Energy
Office of Scientific and
Technical Information
P.O. Box 62
Oak Ridge, TN 37831

For:

Grant Number DE-FG08-94NV11502

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

EXECUTIVE SUMMARY

This report describes the progress achieved during the period May 1, 1994 through July 31, 1996.

During this period, the different subjects studied were:

- a) Improvements in zone refining experiments to establish optimum refining parameters.
- b) Development of surface reflection spectroscopy as a method to measure crystal surface temperature; preliminary results on applicability on CdTe material.
- c) Atomic Force Microscopy studies in the contact mode.
- d) Optical Methods for Measuring Iodine Vapor During Physical Vapor Transport of HgI_2
- e) Establishment of a Bridgman melt growth facility at Fisk University

08

"Mercuric Iodide Research and Development in Support of DOE Historically Black Colleges and University Program"

A) Improvements in zone refining experiments to establish optimum refining parameters

1) Zone refining experiments

The zone refining technique is one of the steps used during the purification of the mercuric iodide starting material. It is presently being performed in a laboratory built apparatus that includes a narrow (2.5 cm) high temperature heater. The lead iodide material is loaded in silica ampules, evacuated and sealed. After ≈ 100 passes at 1.5 cm/h, the process will be stopped and the HgI_2 ingot will be removed. The central part of the ingot is the purest part of the ingot (impurities having a distribution coefficient differing from unity will accumulate at the extremities of the ingot).

New modifications have been made in the experimental setup to allow for backfilling the ampules with an atmosphere of inert gas. In the initial experiments we will use approx. 300-400 torr of Ar. This additional procedure will improve the experimental conditions by avoiding the sublimation of material during the melting process.

Modifications have been made in the experimental setup to allow for vertical refining. Efficient mixing of the fluid, as it occurs under the conditions of gravity induced convection, is crucial to zone refining process. In the vertical configuration the convection is dramatically increased and will result in an improved separation of impurities. Several technical difficulties had to be overcome (better thermal insulation of the ambient oven, improved heater configuration to avoid smearing (broadening) of the thermal profile. The setup was successfully tested and two experiments were completed.

2) Impurity Distribution of Zone-Refined Mercuric Iodide by ICP-AES

Mercuric iodide single crystal is being developed for x-ray and gamma ray detectors applications where high-purity starting materials is required. Zone refining processing has been proven to be a effective step in the purification of large amounts of mercuric iodide for crystal growth. In this study we used the Inductively Coupled Plasma-Atomic Emission Spectroscopy, ICP-AES (performed at Sandia National Laboratories, with one of the Fisk students Leroy Salary participating in the measurements) to identify and determine the distribution of impurity

concentrations along the ampule after zone-refining mercuric iodide. The results shows that for Ag, Cu, Fe, Mg, Ca, Zn and Al, the zone-refining process does sweep the impurities to the last-to-freeze zone, due to an effective distribution coefficient, $k < 1$. For Na, Ni and Pb the concentration gradient seems to be fairly independent of the position along the ingot.

B) Development of surface reflection spectroscopy as a method to measure crystal surface temperatures; preliminary results on applicability on CdTe material

Previous evaluation of the SPEX Triplemate spectrophotometer equipped with a multichannel CCD detector revealed that although much faster accumulation times are required to obtain reflectivity spectra, the signal to noise ratio was still limited by the saturation of the CCD detector at levels of 6×10^5 counts per channel.

The operation of the instrument in a new upgraded mode that provides data averaging has shown that by averaging 20 spectra, (each with an integration time of 1 sec) an improvement by almost a factor of two in the error of the determination of the peak position of the reflectivity peak (and therefore in the determination of the surface temperature) was achieved.

A heat controlled optical cell was designed and built and evaluated for reflectivity measurements at elevated temperatures. A freshly polished CdTe sample was placed inside a pyrex ampule equipped with an optically flat window. Initial data was taken around 100 °C. The results show that the Reflectance Spectroscopy Thermometry (RST) is a promising technique for materials other than HgI_2 .

C) Atomic Force Microscopy (AFM) studies in the contact mode

Atomic force microscopy (AFM) are underway to characterize the surface of semiinsulating mercuric iodide and lead iodide crystals. The high vapor pressures of these compounds prohibit the use of techniques that require high vacuum conditions. Intrinsic defects and defects induced by surface preparation were imaged with high resolution. Both mercuric iodide and lead iodide are very soft materials and under certain conditions, mechanical deformations or material

redistribution during AFM scanning in the contact mode were found to occur. Efforts were made to minimize tip induced modifications and image the effects of aging at ambient temperature and atmosphere. The conclusions are that some surface modifications always occur and result in indentations as well as cleavage step motion.

D) Optical Methods for Measuring Iodine Vapor During Physical Vapor Transport of HgI_2

Optical methods have been established for in-ampoule measurements of the iodine vapor concentration during the growth of mercuric iodide (HgI_2) single crystals by physical vapor transport (PVT). Significant concentrations of iodine vapor, which can vary during the growth period, occur in some ampoules. The absorptivity of iodine vapor at 514 nm is $7.7 \cdot 10^5 \text{ cm}^2 \text{ mol}^{-1}$. Differential Scanning Calorimetry (DSC) measurements correlate with vapor absorption and indicate the presence of free crystalline iodine in vapor-grown HgI_2 .

Consider a transparent ampoule containing an absorbing medium. The transmitted intensity I is related to the absorbance A by $A = \ln(I_0/I)$, where I_0 is the intensity transmitted when there is no absorption. The absorbance and the vapor density are related in the conventional way by Beer's Law,

$$A = \alpha' d \rho \tag{1}$$

where α' is the absorptivity which depends only on the type of vapor, d is the path length, and ρ is the vapor density. In circumstances where Beer's Law is not obeyed, α' can be taken as having some apparent dependence on vapor density, $\alpha'(\rho)$.

Using the well justified assumption that iodine is an ideal gas at the concentrations of interest,⁽¹⁰⁾ the partial pressure P and Kelvin temperature T are related by $P = \rho RT/M$, where R is

the gas constant and M is the molar mass of I_2 . The partial pressure of I_2 over solid iodine has been determined experimentally ⁽¹⁾ and is given by

$$\log_{10}[P(\text{torr})] = 9.9543 - 3103.7/T \quad (2)$$

The absorbance, $A = \ln(I_0/I)$, can be measured for a set of calibration ampoules of known dimension d and iodine vapor densities ρ . A plot of A versus ρ yields a master curve $A(\rho)$ from which unknown vapor densities in experimental ampoules can be obtained from measurements of their I_0/I values. If Beer's Law is obeyed as in equation (1), the curve is linear and passes through the origin, and the absorptivity α' may be found from the slope.

The constant transmission above the saturation temperature, where the density is constant, shows that the absorption spectrum depends explicitly on density and not on temperature, which affirms a basic assumption of the absorption method. The saturation temperature T_s is related to the iodine mass m through the ideal gas law and equation (2) by

$$m = \frac{MV}{RT_s} \cdot 10^{9.9543 - \frac{3103.7}{T_s}} \quad (3)$$

where V is the ampoule volume and R is in appropriate units. The known behavior of iodine as an ideal gas, along with the wide applicability of Beer's law, generally would predict a linear dependence. The line of best fit at low densities has been obtained and is given by equation (4),

$$A = 7.3 \times 10^{-3} \rho \quad (4)$$

where ρ has units of $\mu\text{mol l}^{-1}$.

The absorptivity α' of iodine vapor may be calculated from equations (1) and (4), using the representative value of 9.6 cm for the ampoule diameter, and is given by $\alpha' = 7.7 \cdot 10^5 \text{ cm}^2 \text{ mol}^{-1}$.

E) Establishment a Brigman melt growth facility at Fisk University

Using equipment donated by DoE originating from the former EG&G/EM Santa Barbara Operations a crystal growth facility using the Brigman technique was established. The facility was already used by 4 undergraduate summer program students during the months of June and July 1996.

This facility can be used to produce single crystals of semiconductors having a melting point of up to 1200 C. The systems were tested in the growth of PbI_2 crystals.