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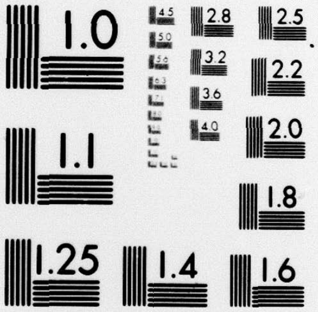

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We have grown crystalline epitaxial layers of mercury cadmium telluride from a mercury-rich melt by the method of constant temperature current controlled liquid phase epitaxy (CCLPE). CCLPE is an attractive method of crystal growth for mercury cadmium telluride because it has the potential for achieving better uniformity than bulk cryatal techniques. In addition it can be used for direct growth of p-n junctions by addition of suitable dopants. The lower growth temperature compared to bulk growth methods is

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expected to result in fewer vancancies.

Growth was achieved under conditions where the substrate was hotter than the source as well as under circumstances where the substrate was colder than the source. This indicated that the mass transport was driven by electromigration rather than the Peltier effect.

Several layers were grown to a thickness of 30-100 microns. Best results were obtained on (111) oriented substrates. These layers were studied micrographically and with the use of X-ray diffraction methods.

One 500 micron thick layer was also investigated by the electrolyte electroreflectance method in order to determine composition and homogeneity. This piece was found to have a mole fraction of cadmium telluride equal to 0.1. This represented a considerable mercury enrichment over the substrate and source. The variation in mole fraction of cadmium telluride over the surface of the sample ~~($\approx$1 cm^2)~~ was approximately 0.03. Another layer of about 100 micron thickness grown at 260°C was found by the electrolyte electroreflectance method to have a composition similar to the source and substrate.

(approx. 1 sq cm)

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Report

AFOSR-78-3730

The objective of this research project was to improve the quality of epitaxial layers of $Hg_{1-x}Cd_xTe$ and to develop new methods of characterizing the homogeneity.

We have grown crystalline epitaxial layers of $Hg_{1-x}Cd_xTe$ from a Hg-rich melt by the method of constant temperature current controlled liquid phase expitaxy (CCLPE). Growth was achieved by passing a current through a liquid Hg melt contained between two crystals of $Hg_{1-x}Cd_xTe$ ($x \approx 0.35$) which act as source and substrate, respectively. Growth was achieved under conditions where the substrate was hotter than the source as well as under conditions where the substrate was colder than the source. This indicated that the mass transport was driven by electromigration rather than the Peltier effect. Best results were obtained on (111) oriented substrates. One 500μm thick sample was investigated by the electrolyte electroreflectance (EER) method and found to have $x \approx 0.1$ and a variation $\Delta x \approx 0.03$ across the surface. Hence since the source and substrate had $x \approx 0.35$ this exitaxial layer was considerably enriched in Hg. A layer of approximately 100μm thickness was found by the EER technique to have composition ($x \approx 0.35$) similar to that of source and substrate. This latter sample was grown at a somewhat lower temperature (260°C) in relation to other layers (280-300°C).

The crystal growing cell consists of a cylindrical piece of fused quartz tubing with polished ends. The liquid Hg is contained in the growth cell by placing two flat, polished crystals of $Hg_{1-x}Cd_xTe$ against these polished ends. One of the crystals serves as the source and the other as the substrate when a current is passed between them through the liquid Hg "melt." The crystals are held in place by two flat stell springs which press against graphite

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holding cups in order to prevent possible contamination of the crystals at elevated temperatures. The steel springs and graphite holders also serve as the electrical connections. Connected to the cylindrical piece is a somewhat larger round piece of quartz which acts as a reservoir for the mercury. A considerable portion of the mercury vapor condenses at the top of this bulb. This bulb in turn is attached to a vertical section of quartz tubing which leads to a water-cooled reflux condenser, so that all the evaporating Hg is returned to the "melt." The pressure inside the cell is maintained at one atmosphere using flowing argon gas. This entire assembly is surrounded by an argon-filled quartz flask in order to contain any Hg which might escape if the cell were to fail. This flask is also vented through a separate water-cooled condenser. The output from both condensers is passed through an ice-cooled trap for additional protection against the hazards of the Hg vapor.

The outer flask fits into a 500 watt furnace controlled at a given temperature. The temperature is sensed by a temperature control thermocouple. The stability of the temperature controller is ± 0.1°C. Because the system is designed to operate below the boiling point of mercury (360°C) the solidus temperature for $Hg_{0.8}Cd_{0.2}Te$ ($\approx$ 680°C) (1) cannot be achieved. For the process to work, (a) the temperature must be high enough so that an appreciable amount of the source crystal can dissolve in the melt, and (b) transport of these solutes should take place across the cell in a reasonable time. We have found that a measurable amount of each crystal dissolves in the Hg ($\approx$ 0.5% solute) even at temperatures as low as 200°C, and that about half a millimeter of the source is dissolved away at the normal operating temperature of 280-300°C ($\approx$ 5% solute).

The procedure, once the apparatus is assembled, is to heat about 300°C (somewhat above the growth temperature) in order to establish a saturated solution by partial dissolution of source and substrate wafers. The temperature is then stabilized for 2 or 3 hours before any current is applied to the cell. The current is first applied in the reverse direction to make sure that the surface material from the substrate is dissolved away, creating a fresh interface. The dissolution process is much faster than growth so that very little material is deposited on the source during this procedure. The current is then applied in the forward direction for a period of up to 5 days, while maintaining a constant furnace temperature. The furnace is then cooled while argon gas is blown rapidly on the surface of the melt to crystallize the solute in the liquid. We have found that for the case of a similar heating cycle but without applied current there is no observable epitaxial growth. The dissolved material then nucleates small crystallites through the cell.

In order to detect the small temperature difference, ΔT, across the liquid and monitor it continuously throughout the growth process, a pair of differential themocouples was attached to the walls of the fused quartz cell near the solid-liquid interface. We will adopt the convention that ΔT is positive when the anode is hotter than the cathode. The source-to-substrate distance was kept constant at 7.0 mm, but the thicknesses of the source and substrate were varied from 0.5 mm to 3 mm. Two different diameters of graphite holders (2.0 cm and 1.3 cm) were used. Unless other wise specified, the configuration was always made as symmetrical as possible, by matching the sizes of the crystal and the holder at the anode with those at the cathode. However, it was possible to introduce a deliberate assymmetry by replacing one of the holders with another of a different size.

Whenever the current was switched on, or increased in a step, we observed a negative transient ΔT with a decay time of a few seconds. The steady state ΔT was also negative and increased linearly with current for small currents. For apparently symmetrical configurations, a weak quadratic dependence on current was observed above about 20 A-cm^{-2}. The sign of the quadratic component changed run to run and appeared to be the result of small accidental deviations from symmetry. For very thin ($\gtrsim$ 1.0 mm) substrate and source wafers in a symmetric configuration, ΔT was less than 0.1°C. For slices as thick as 3 mm, steady state temperature differences as large as 0.5°C were measured, using currents up to 28 A-cm^{-2}. When the configuration was made assymmetric by using a 2.0 cm diameter holder at the cathode and a 1.3 cm diameter holder at the anode, the quadratic component of ΔT became large and positive, so that it offset the linear component for currents as small as 5 A-cm^{-2}. This effect allowed one to carry out growth runs with a positive ΔT. In <u>all</u> cases dissolution occurred at the anode, regardless of the sign of ΔT.

We interpret the low-current linear ΔT as a Peltier cooling of the anodic interface. The dependence of ΔT on the thickness of the Hg/$Hg_{1-x}Cd_xTe$ slices shows that the thermal conductances through the crystal slices are important factors affecting the steady state temperature profile of the cell, as in the case of CCLPE of GaAlAs. The quadratic component of ΔT at higher currents was probably the result of assymetric Joule heating of the crystal wafers and their holders. The fact that growth can occur at the anode even with a positive ΔT indicates that the Peltier effect is not sufficient to explain the observed growth (though it may play a role when the electrodes are symmetric). The predominant effect seems to have been electromigration of dissolved species across the cell, producing a saturated solution at the anode while etching away the cathode.

Crystalline layers were grown on oriented (100), (110) and (111) substrate faces ($\pm 1^{\circ}$) as well as on randomly oriented and polycrystalline surfaces. Best results were obtained on (111) oriented substrates. In all cases the source and substrate material was $Hg_{1-x}Cd_xTe$ with $x \gtrsim 0.3 - 0.4$. The source (substrate) surfaces were polished with 12μm, 0.5μm and 0.03μm alumina powder, etched in a stirred solution of bromine and methanol (ratio of 1:10) for about 1 minute and then rinsed thoroughly in methanol.

Using the method of CCLPE we have grown a number of crystalline layers of $Hg_{1-x}Cd_xTe$. The main defects in the first films appear to be associated with (a) the fialure of the mercury to wet the substrate in some spots and (b) the uneven melt back of the substrate before the initiation of growth. Subsequently the former problem was solved by evacuating the growth cell before introducing the Hg thus minimizing the formation of the bubbles which were responsible for the lack of welting.

A number of crystalline layers of thickness 30-100μm were grown as well as one layer of 500μm thickness. This latter sample was investigated by the EER topographical method and found to have $x \approx 0.10$ and a variation $\Delta x \lesssim 0.03$ across the surface. Since the source and substrate materials had $x \approx 0.35$ this epitaxial layer was enriched in Hg. A layer of approximately about 100 μm thickness grown at a somewhat lower temperature (260°C) in relation to the 500 μm sample (280°C) was found by the EER method to have a composition similar to the source and substrate ($x \approx 0.35$).

List of Publications

1. "Current Controlled Liquid Phase Epitaxial Growth of $Hg_{1-x}Cd_xTe$" by P.E. Vanier, F. H. Pollak and P.M. Raccah, J. Electronic Materials 9, 153 (1980).

Personnel

Principal Investigator - F. H. Pollak

Research Associate - L. I. Berger

Scientific Interactions

We have established excellent working relationships with a number of workers in the field. In particular we have had close contact with the materials group (Drs. P. Bratt and A. Lockwood) at the Santa Barbara Research Center. They have enthusiastically provided us with many of the samples used in our work. We are in close contact with them and have sent them several technical reports, particularly on the EER topographical investigation of stoichiometry in not only $Hg_{1-x}Cd_xTe$ but also $InAs_{1-x}Sb_x$ and $PbSn_{1-x}Te_x$. We have also been in contact with the $Hg_{1-x}Cd_xTe$ groups at A.D. Little and Honeywell. The latter group has provided us with some $Hg_{1-x}Cd_xTe$ for compositional analysis and a technical report has been sent to them based on our results. In addition, we have examined samples of $Hg_{1-x}Cd_xTe$ from Prof. G. Nimtz from the University of Koln. Discussions on this project have been held with Prof. Roy Cornely of the New Jersey Institute of Technology and Prof. S. Ushioda of the University of California at Irvine.

Dr. L. I. Berger, research associate on this project during the past year, is presently at the New England Research Center (NERC) in Sudbury, Mass. Dr. Berger has examined several $Hg_{1-x}Cd_xTe$ samples fabricated at NERC by the EER technique at our laboratory. We have also established a relationship with Prof. M. Averous of the University of Montpelier in France. One of his staff will shortly visit our laboratory.