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GROWTH AND HOMOGENEITY CHARACTERIZATION OF MERCURY CADMIUM TELL--ETC(U)

JAN 79 F POLLAK

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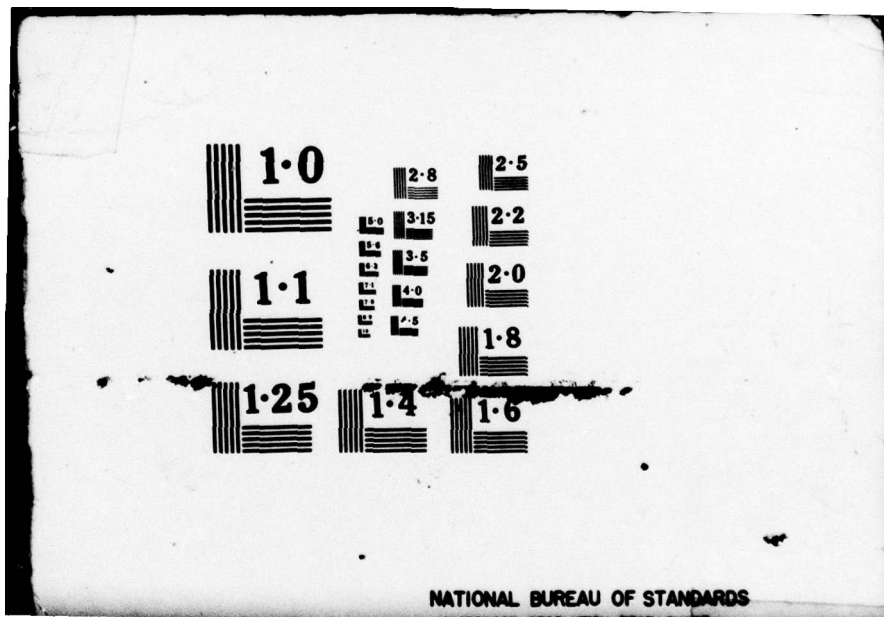
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. The films grown were of thicknesses from 10 microns to over 100 microns. Regular arrays of facets with a common orientation all over the film indicated that the deposited material was epitaxially grown rather than randomly oriented. The crystal structure of orientation of the grown material were studied by X-ray diffraction and found to be the same as in the substrate. By the electrolyte electroreflectance technique, it was shown that the grown material had a mole fraction of cadmium telluride equal to 0.1 ± 0.01 . This represented a considerable mercury telluride enrichment over the substrate and the source. The compositional homogeneity of the grown layer was comparable to that seen in some of the better quality crystals analyzed in this laboratory.

In the second phase of this program a new, larger growth cell (6 mm in diameter) was used to produce layers with areas a factor of 4 larger than those mentioned above. By the use of differential thermocouples embedded in the walls of the fused quartz cell, the mechanism of material transport across the cell has been investigated. This study has shown that growth will occur at the positive end of the cell even if it is slightly hotter than the negative end. The conclusion is that growth is not driven by the Peltier effect, as in the case of CCLPE of gallium aluminum arsenide, but rather is the result of electro-migration of the dissolved species in the liquid mercury.

Our experiments have shown that the smoothest layers are grown on (111) substrates. We suspect that there may be differences in growth rates and morphology between layers grown on "A" - and "B" -type (111) surfaces. We have therefore attempted to devise a simple and reliable method of distinguishing "A" and "B" faces of mercury cadmium telluride using the amplitude and phase of the electroreflectance signal, which is highly sensitive to changes in surface potential. This part of the investigation has shown some interesting new results.

Utilizing electrolyte electroreflectance, we have developed a unique approach for determining the variations in composition x across the face of binary and ternary alloy semiconductors. This technique is based on the fact that the energies of features in the optical spectra of semiconducting alloys depend on x in a continuous manner. Any shift in energy of a particular electroreflectance peak is measured using a small scanned light spot. Corresponding variations in x can be determined to within about 1% with a spatial resolution of about 100 micron. This technique is nondestructive and can readily be employed under atmospheric conditions at room temperature.

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Report

The objective of this research project was to improve the quality of crystalline layers of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and to develop new methods of characterizing the homogeneity. We have developed the method of current controlled liquid phase epitaxy (CCLPE) from mercury-rich solutions. It has been determined that the dominant mechanism of solute transport across the growth cell is by electromigration rather than by Peltier-induced temperature gradients. Only by understanding these processes is it possible to choose the optimum conditions of temperature, current and cell geometry necessary for the growth of highly homogeneous layers. Another question which we addressed was whether the growth rates and crystal quality were different for layers grown on (111)A and (111)B oriented substrates. This led us to search for a new method of distinguishing "A" from "B" faces of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, and we have made significant progress in this endeavor using electrolyte electroreflectance (EER). In addition the technique of EER has been developed into a powerful tool for evaluating the topographical features of compositional homogeneity in binary and ternary semiconductors.

We have grown crystalline layers in a new, larger growth cell, covering a circular region 6 mm in diameter on the substrate to a thickness of 30-50 μm . In the CCLPE method, a direct current is passed between two crystals of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ in contact with a pool of liquid mercury. A certain amount of each crystal dissolves in the mercury until a saturated solution is obtained at the chosen furnace temperature ($\approx 280^\circ\text{C}$). The electric current then causes one crystal to grow while the other continues to dissolve. Two independent mechanisms have been proposed to explain this current-dependent mass transport. First, the Peltier effect at the solid-liquid junctions should produce a cooling effect at one crystal surface and a heating effect

at the other. The resulting small gradients of temperature and composition could cause transport of solutes either by diffusion or by convection. A second possibility is that of electromigration, which could occur even in the absence of a temperature gradient.

We have cemented a pair of differential thermocouples to the walls of the fused quartz cell near the solid-liquid interfaces in order to detect small temperature gradients across the cell and monitor them continuously throughout the growth process. We have observed that whenever the current is switched on, or increased in a step, there is a transient temperature gradient with the positive end of the cell becoming cooler than the negative end. This lasts for a few seconds and then a steady state is gradually approached in which, for small currents, the magnitude of the temperature gradient is smaller than the transient effect, but in the same direction. For larger currents, the steady state temperature gradient can be larger than the transient, and can have the opposite sign, depending on the geometry of the source and substrate crystals and their graphite holders.

This behavior is explained as follows. The thermocouples first detect the cooling of the positive end of the cell due to the Peltier effect at the solid-liquid junction. This gives the sharp initial transient signal which gradually diminishes as heat is conducted across the cell. At the same time, there is a reverse Peltier effect on the back surfaces of the substrate and source crystals where they make contact with the graphite holders. It takes a few seconds for a steady state pattern of heat flow to be set up, after which the temperature gradient across the liquid is much less than it was initially. For very thin samples (~ 1 mm) it is not possible to maintain much temperature difference between opposite faces of the sample, and the net Peltier effect measured in the cell is small. For samples as thick as 3 mm, steady state Peltier temperature differences as large as 0.5°C were measured.

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For small currents, the temperature difference increased linearly with current. For larger currents, the temperature gradient was dominated by Joule heating of the substrate source, and holders, which were not always symmetric. This effect was quadratic with current and could be in the opposite direction from the Peltier effect.

Crystalline layers were grown under a variety of conditions, using two different sizes of sample holders to vary the steady state temperature gradient for a fixed current. It was found that material was always dissolved from the negative end of the cell and transported to the positive end, depositing an epitaxial layer. This occurred even if the positive end was slightly (0.3°C) hotter than the negative end. This demonstrated that the dominant current-dependent transport mechanism was not via a Peltier-induced temperature gradient, and in fact did not require a temperature gradient at all. Rather, the crystal growth was the result of electromigration of dissolved species across the cell.

One feature of the crystal growth which seemed to depend on the temperature gradient in the cell was the flatness of the surface of the grown layer. The results so far appear to indicate that if the substrate is made hotter than the melt, the growing interface becomes unstable and tends to form a rough surface, even on a (111) oriented substrate. There may, however, be other variables to consider. For instance, there may be differences in growth rates and surface morphology between layers grown on (111)A and (111)B surfaces, which might explain some of the variations observed.

In order to explore this question further we investigated various methods of distinguishing the "A" and "B" faces of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. The common etchants used on II-VI and III-V compound semiconductors do not seem to give reproducible results, and it has been reported that the preferential etching of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

depends on the composition. X-ray methods are extremely difficult, requiring very subtle techniques in order to separate out the scattering by the different types of atoms. We therefore attempted to devise a new method of distinguishing "A" and "B" faces using electrolyte electroreflectance (EER).

Each sample was cut with (111) faces, polished on both sides, and mounted so that both surfaces were exposed to the electrolyte in the optical cell. EER spectra were then plotted for both sides of the sample under the same conditions and the amplitudes of the peaks were compared. In all of the samples measured, including some other semiconductors with the zincblende structure, such as GaAs and InSb, there was a marked difference in peak amplitude between the two sides of a given sample. This resulted from the different degree of band-bending on the "A" and "B" faces. In fact, one sample of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ showed a complete reversal of the sign of the EER signal, indicating that one surface was inverted, having the opposite sign of charge carrier at the surface than the bulk. This technique promises to be generally useful for many compound semiconductors with the same structure.

Utilizing electrolyte electroreflectance, we have developed a unique approach for determining the variations in composition x across the face of binary and ternary alloy semiconductors. This technique is based on the fact that the energies of features in the optical spectra of semiconducting alloys depend on x in a continuous manner. Any shift in energy of a particular electroreflectance peak is measured using a small scanned light spot. Corresponding variations in x can be determined to within about 1% with a spatial resolution of about 100 μm . This technique is nondestructive and can readily be employed under atmospheric conditions at room temperature.

List of Publications

1. "Variations in Stoichiometry of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ by Electrolyte Electroreflectance: A Topographical Investigation", P.E. Vanier, F. H. Pollak and P.M. Raccach, presented at the Topical Meeting on Optical Phenomena in Infrared Materials, Annapolis, Md. 1976; Appl. Optics 16, 2858 (1977).
2. "Variations in Stoichiometry of Binary and Ternary Semiconductors: A Topographical Investigation" by F.H. Pollak, C.E. Okeke, P.E. Vanier and P.M. Raccach, J. Appl. Physics 49, 4216 (1978).
3. "Current Controlled Liquid Phase Epitaxial Growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ", P.E. Vanier, F.H. Pollak and P.M. Raccach, submitted to Journal of Electronic Materials.

PERSONNEL

Principal Investigator - F.H. Pollak

Co-principal Investigator - P.M. Raccach (now at Univer. of Ill.-Chic. Circle)

Co-principal Investigator - P.E. Vanier

Technicians- S. Wasserman and R. Wright

Scientific Interactions

Prof. F. Pollak attended the 1977 Device Research Conference at Cornell University and presented a paper entitled "Topographical Investigation of Variations in Stoichiometry in $\text{Ga}_{1-x}\text{As}_x$ and Carrier Concentrations in GaAs Using Electroreflectance" with authors F.H. Pollak, C.E. Okeke, P.E. Vanier and P.M. Raccach.

In March 1977, Dr. Vanier and Professor Pollak attended the annual meeting of the American Physical Society in San Diego, Ca. Informal discussions were held with a number of scientists at the meeting.

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 $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ but also $\text{InAs}_{1-x}\text{Sb}_x$ and $\text{PbSn}_{1-x}\text{Te}_x$. In addition, we visited them in March 1977 and gave a seminar on our work in both the areas of crystal growth and topographical composition determination. We have also been in contact with the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ groups at A.D. Little and Honeywell. The latter group has provided us with some $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ for compositional analysis and a technical report has been sent to them based on our results. In addition, we have examined samples of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ from Prof. G. Nimtz from the University of Koln.

We have visited Dr. Daniele at Philips Laboratories at Briarcliff Manor, and held useful discussions with him on the LPE crystal growth technique. We have also discussed this project with Prof. Roy Cornely of the New Jersey Institute of Technology and Prof. S. Ushioda of the University of California at Irvine.

In June 1978 Prof. Pollak delivered a paper entitled "Current Controlled Liquid Phase Epitaxy of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ " (co-authors P.E. Vanier and P.M. Raccah) at the 20th Annual Electronics Materials Conference in Santa Barbara, California. At this meeting conversations were held with a number of scientists. Prof. Pollak also visited Dr. Art Lockwood at Santa Barbara Research Center.

Patents

A.U.S. Patent Application No. 855,831 entitled METHOD AND APPARATUS FOR MEASURING VARIATIONS IN COMPOSITION IN BINARY AND TERNARY SEMICONDUCTORS UTILIZING ELECTROLYTE ELECTROREFLECTANCE (F. Pollak and P.M. Raccah) has been filed by Yeshiva University with the United States Patent and Trademark Office.