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VAPOR TRANSPORT CRYSTAL GROWTH OF MERCURY-CADMIUM-TELLURIDE IN MICROGRAVITY (INTERIM REPORT)

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ABSTRACT

Two epitaxial growth experiments of $Hg_{1-x}Cd_xTe$ layers on (100) CdTe substrates in closed ampoules using HgI_2 as a transport agent have been performed during the USML-1 Mission. The characterization results to date demonstrates a considerable improvement of the space-grown epitaxial layers relative to ground-control specimens in terms of morphology, compositional uniformity, and structural micro homogeneity. These results show the effects of microgravity and of fluids dynamic disturbances on ground on the deposition and growth processes. The continued analysis of this technologically important system is designed to further elucidate the observed crystallographic improvements and their relation to mass flow.

INTRODUCTION

Our earlier chemical vapor transport (CVT) experiments of germanium-chalcogenide systems in microgravity environment demonstrated the feasibility of the closed tube vapor transport method for crystal growth in space. The results of the Skylab [1] and Apollo-Soyuz [2] experiments yielded GeSe and GeTe crystals of considerably improved chemical and structural micro homogeneity. The space grown crystals were also larger than ground based specimens. An important observation of these early experiments were quantitative mass transport rates significantly greater than predicted for diffusion limited conditions in microgravity. As a hypothesis, we proposed that these mass flux anomalies were related to thermal effects of homogeneous gas phase reactions in these multi-component-multi reaction CVT systems [2]. The physical vapor transport (PVT) of the GeSe-Xenon system represents a two-component-single-reaction system essentially without any chemical homogeneous gas phase reactions. Vapor transport crystal growth experiments of the GeSe-Xenon system during the STS-7[3] and D-1[4] missions yielded mass transport rates in excellent agreement with theoretical predictions of diffusive flow and with experimental data for vertical, stabilizing conditions on ground. These observations strongly

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support the validity of our hypothesis concerning the effects of homogeneous gas phase reactions on mass flow. In addition, the STS-7 and D-1[3,4] experiments yielded GeSe single crystals of considerably improved quality and much larger sizes than observed under ground-based conditions.

A more recent reevaluation of the mass transport properties of the GeSe CVT and PVT systems on ground and in microgravity [5] reconfirmed the above conclusions and observations. In addition, the results of numerical modeling of related transport systems [6,7] are consistent with our experimental observations and theoretical explanations of the earlier transport experiments.

The investigation of the vapor transport and crystal growth properties of the $Hg_{1-x}Cd_xTe$ alloys is based on the above experience with such systems on ground and in microgravity environment. The technologically useful electro-optical properties of $Hg_{1-x}Cd_xTe$ alloys in the 3-5 and 8-14 μm range are based on the formation of continuous series of solid solutions with a nearly linear change in lattice parameters and corresponding changes in the band gap energy of this material. Because of the significant differences in vapor pressure of the constituent elements and binary components of this system, and because of the solid-liquid phase diagram of the $Hg_{1-x}Cd_xTe$ solid solution system, growth of $Hg_{1-x}Cd_xTe$ single crystals presents considerable problems. Growth from the melt is associated with inherent segregation effects. Physical vapor transport requires the use of multiple sources to adjust the vapor pressures. And the employment of CVD and MOCVD techniques requires complex instrumentation which is presently not suitable for space experimentation. Based on our extensive experience in vapor transport properties of metal chalcogenide systems, the concept of chemical vapor transport of $Hg_{1-x}Cd_xTe$ in closed ampoules using a single source material and a transport agent was developed in our laboratory.

I. SCIENTIFIC AND TECHNOLOGICAL BASIS

Our earlier chemical vapor transport and crystal growth studies of the $Hg_{0.8}Cd_{0.2}Te$ system [8] demonstrated that bulk crystals could be grown in closed ampoules using a single source material and HgI_2 as a transport agent. Mass transport rate studies of the $Hg_{1-x}Cd_xTe$-HgI_2 system (x=0.2 for the source material) as a function of transport agent pressure and for different orientations of the density gradient relative to the gravity vector were performed [8].. The results showed that the chemical structural microhomogeneity of the crystals are considerably affected by gravity-driven convection. The growth of single crystals of $Hg_{1-x}Cd_xTe$ from the vapor phase appears to be very sensitive to even relatively small fluid dynamic disturbances. A first order thermodynamic analysis of the $Hg_{0.8}Cd_{0.2}Te$-Iodine transport system for different compositions of the source material [9,10] yielded estimations of the diffusive mass transport rates. The computed and experimental mass transport rates [9,10]are in close agreement. In connection with additional CTV studies of the $Hg_{0.8}Cd_{0.2}Te$-H_gI_2 vapor transport system

[11], the transport model developed earlier [9,10] was further tested and extended for different conditions. Experimental results in terms of mass transport rates and compositions of the grown crystals are in close agreement [11]. This confirms the validity of the model applied to the CVT process of this system.

The above observations and results [8-11] provided the basis for the growth of epitaxial layers of $Hg_{1-x}Cd_xTe$ by the closed tube chemical vapor transport technique. Exploratory studies of the epitaxial growth of $Hg_{1-x}Cd_xTe$ demonstrated the feasibility of the chemical vapor transport technique for this purpose [12]. The characterization of the $Hg_{1-x}Cd_xTe$ layers grown on CdTe substrates [13,14] revealed good single crystallinity of the layers and electrical properties comparable to reported data.

More recent detailed investigation under this program of the vacancy concentration and P-T phase diagrams of the $Hg_{0.8}Cd_{0.2}Te$ and $Hg_{0.6}Cd_{0.4}Te$ systems were performed employing dynamic mass-loss measurements [15]. The results of these investigations yielded quantitative Hg partial pressures at the phase boundaries and within the homogeneity region. In addition, the enthalpy of formation of singly-ionized metal vacancies was obtained from these measurements[15]. Analogous investigations of the $Hg_{0.8}Zn_{0.2}Te$ system yielded the corresponding Hg partial pressures and enthalpy of formation of singly-ionized metal vacancies for this system [16]. From a comparison of the $Hg_{0.8}Cd_{0.2}Te$ and $Hg_{0.8}Zn_{0.2}Te$ systems, the influence of Cd and Zn on the bonding in HgTe could be ascertained. Theoretical predictions of the bond strengthening (weakening) effects of alloying HgTe with Zn or Cd are consistent with our observations [15,16]

The above information was used for the further improvement of the crystal growth of $Hg_{1-x}Cd_xTe$ by chemical vapor transport. Employing a combined CVT-seeding technique, bulk crystals of $Hg_{0.8}Cd_{0.2}Te$ of good chemical and structural homogeneity could be grown [17]. Possible origins of the subgrain structure were examined

Continued detailed investigations of the epitaxial growth of $Hg_{1-x}Cd_xTe$ on CdTe substrates [18] revealed the influence of growth temperature, of substrate orientation, and of HgI_2 pressure. Layers of nearly uniform composition and low etch pit densities were obtained. The growth temperature and HgI_2 pressure have significant effects on the layer morphology and composition [18].

Similar investigations of the epitaxial growth of $Hg_{1-x}Cd_xTe$ were performed using different source material compositions, different growth temperatures and HgI_2 pressures [19]. As predicted from the above vapor pressure measurements [15], the source composition has a significant effect on the mass transport and growth rates of the system [19]. From these measurements, suitable experimental parameters for the growth of epitaxial layers of desired composition can be deduced.

The combined results of the above ground-based investigations provide the scientific and technological basis for microgravity experiments of this system. The ground based results can be summarized as follows:

1. Bulk single crystals of $Hg_{0.8}Cd_{0.2}Te$ can be grown by CVT using a single source material in closed ampoules.
2. Convection effects on the chemical and structural microhomogeneity of bulk crystals are established.
3. Epitaxial layers of $Hg_{0.8}Cd_{0.2}Te$ on CdTe substrates have been grown by CVT using a single source and HgI_2 as a transport agent.
4. Convection effects on uniformity and properties of epitaxial layers have been observed.
5. Based on a thermodynamic analysis of the $Hg_{0.8}Cd_{0.2}Te$-HgI_2 system, diffusion controlled mass fluxes and the composition of bulk crystals can be predicted.
6. The above results have been used for the development of crystal growth experiments in microgravity environment.
7. The above results provided the basis for the definition of experimental parameters for the vapor growth of $Hg_{1-x}Cd_xTe$ epitaxial layers on CdTe substrates during the USML-1 Mission.

II. USML-EXPERIMENTS

A. Experimental Conditions and Procedures

The growth ampoule consisted of a fused silica tube of about 15 mm outer diameter and 10 cm length. The source material slug was located at the rounded end of the ampoule and was firmly attached to the ampoule wall. The (100) CdTe substrate was located at the other flat end of the ampoule on a very flat sapphire disc. In order to maintain the substrate in its proper position and to seal the loaded growth ampoule under high vacuum, a double-ampoule configuration was employed for these experiments. The loaded and sealed ampoule was inserted into a metal cartridge and instrumented with five K-type thermocouples to monitor the temperature of the source, and in between at all times.

The ampoule-cartridge assembly was inserted in the crystal growth furnace (CGF) where the heat-up, crystal growth and cool-down occurred according to time-lines developed during the ground-based studies and GCEL test experiments. The proper positions of the thermocouples and the physical integrity of the entire cartridge-ampoule assembly were confirmed by X-ray diffraction photography before and after the flight experiments.

The growth conditions of the flight experiments are as follows:

Flight Experiment RPI-1:

Source Material:	$Hg_{0.4}Cd_{0.6}Te$
HgI_2 Pressure	~0.01 atm
Growth Time:	8.1 hours
Nominal Growth Temperature:	545°C
Nominal Source Temperature:	593°C

Flight Experiment RPI-2:

Source Material:	$Hg_{0.4}Cd_{0.6}Te$
HgI_2 Pressure:	~0.01 atm
Total Growth Time:	6.4 hours
Nominal Growth Temperature:	545°C
Nominal Source Temperature:	593°C

B. Results and Discussion

The results to date of our two USML-1 experiments are based on optical and scanning electron microscopy, on IR spectroscopy, on electron microprobe (WDS) analysis, on X-ray diffraction Laue and rocking curve measurements, and on Synchrotron investigations.

The present results are summarized below.

B1 Surface Morphology of Epitaxial Layers

A microscopic comparison of the epitaxial layers obtained under ground-control conditions and in microgravity demonstrates an unexpected degree of improvement in surface morphology of the space-grown crystals. The surfaces of the ground-control epitaxial layers have a "wavy" type step-terrace structure. The step heights are in the order of several microns and the widths vary from 20 to about 200 μm. Even the flattest regions of the epitaxial layer obtained during the flight simulation test on ground show uneven and irregular growth steps. At the same magnifications (100-500 X) the epitaxial layers grown in space appear mirror-smooth, i.e., the growth steps cannot be resolved. These differences in surface morphology remain even at much higher magnifications under SEM conditions.

B2 Compositional Homogeneity of Epitaxial layers

Employing infra-red spectroscopy techniques, the overall chemical compositions of the space-grown epitaxial layers are consistent with those of the ground test samples. These observations indicate that any fluid dynamic disturbances on ground are not very large. However, a detailed investigation of the spatial composition distribution (map) reveals considerable differences in uniformity between the ground and space-grown layers. For the entire layers, the compositional differences between local regions are about two to three times smaller for the space than for the ground-control samples. These differences indicate the effects of fluid dynamic disturbances on the deposition and growth processes on ground.

The results of several compositional depth profiles of the (011) cross section of epitaxial layers based on electron microprobe (WDS) analysis show a high degree of composition uniformity of the space-grown layers. In terms of absolute composition, the WDS results are consistent with those of the IR measurements performed in our laboratory.

B3 Structural Homogeneity of Epitaxial Layers

The crystallographic identity of the epitaxial layers grown on ground and in space was determined by X-ray diffraction Laue patterns. The epitaxial layers have a (100) orientation showing a substrate parallel layer growth as expected.

A considerable difference between the crystallographic perfection and uniformity of the space and ground-grown layers was observed based on X-ray diffraction rocking curves. The values of the full-width-half-maximum (FWHM) for the native surfaces of the space-grown layers range from 90-120 arc seconds. Those of the ground-based sample range from about 200-240 arc seconds. The FWHM-values observed for our space-grown layers are equal to or smaller than the best value reported for $Hg_{1-x}Cd_xTe$ epitaxial layers grown by MOCVD techniques on ground. Typical FWHM-values reported in the literature for $Hg_{1-x}Cd_xTe$ are in the order of several hundred arc seconds. In view of the chemical and structural complexity of this growth system, these observations represent a significant crystallographic improvement of the space-grown epitaxial layers relative to those obtained on ground.

B4 Synchrotron Measurements

The results of Synchrotron measurements of the space and ground-grown epitaxial layers reveal a cellular type morphology for both. This kind of structure has been observed for other II-VI and III-V compound crystals. The origin of the cellular structure is not understood at this time for this and other materials. However, it is important to recognize that the material must have a very high degree of crystallographic perfection in order to observe the cellular structure by Synchrotron measurements. This requirement is consistent with the above results of the X-ray diffraction rocking curves which yielded relatively small FWHM-values for the space-grown epitaxial layers. Also consistent with the rocking curve results are the Synchrotron observations of a much larger area of uniform crystallinity of the space grown epitaxial layer compared to the ground sample,

Because of the basic scientific and technological importance of these particular observations, it is highly desirable to continue the Synchrotron measurements on the flight and ground-based epitaxial layers of this material.

III. CONTINUED ANALYSIS AND CHARACTERIZATION OF THE USML-1 Experiments

For several of the above discussed, non-destructive characterization procedures (IR mapping, X-ray diffraction rocking curves, Synchrotron measurements) the facilities employed are not under our control. Therefore, additional analyses of the flight and ground-based samples, involving partly destructive techniques, had to be delayed. These measurements, including cross-section analysis, electrical measurements, and chemical etching, are in progress.

As indicated above, in view of the rather interesting structural investigation and results, it is very desirable to perform additional studies with the objective to further elucidate the origin of the cellular structure.

IV. PRELIMINARY SUMMARY AND CONCLUSIONS

Epitaxial growth experiments of $Hg_{1-x}Cd_xTe$ layers on (100) CdTe substrates by chemical vapor transport in closed ampoules using HgI_2 as a transport agent were performed during the USML-1 Mission in microgravity environment. The results to date demonstrate considerable improvements of the flight samples in terms of surface morphology, chemical microhomogeneity and the degree of crystallographic perfection and uniformity relative to ground-based samples. These improvements are consistent with our earlier predictions concerning the sensitivity of the $Hg_{1-x}Cd_xTe$-HgI_2 vapor transport system to even minute fluid dynamic disturbances on ground. The combined results to date justify the conclusion that these experiments were successful.

Continued analysis and characterization efforts are designed to further investigate the effects of microgravity on the epitaxial growth of this system. Ongoing detailed investigations of the substrate-layer interface revealed new information concerning the effects of microgravity during the initial periods of epitaxial growth. The further elucidation of these phenomena is of basic scientific value and of technological significance. These are important objectives of our experiments proposed for the USML-2 Mission.

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