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Properties of II-VI Semiconductors: Bulk Crystals, Epitaxial Films, Quantum Well Structures, and Dilute Magnetic Systems

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Properties of II-VI Semiconductors: Bulk Crystals, Epitaxial Films, Quantum Well Structures, and Dilute Magnetic Systems

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Preface

The II-VI compound semiconductors possess characteristics which, as a group, are unique. Among the most active areas of investigation in these materials today are blue light emitters based on ZnSe, infrared detectors based on mercury-containing compounds such as HgCdTe, and the properties of dilute magnetic semiconductors. Each of these areas is represented by several papers included in this volume. The symposium at which the papers in this volume were orally presented was attended by 250 researchers from across the globe. Of the nearly 100 papers presented, 69 are contained in these proceedings.

The symposium organizers would like to give special thanks to those institutions which provided financial support: the Air Force Office of Scientific Research, the Army Research Office, the Defense Advanced Research Projects Agency, the Office of Naval Research, and Texas Instruments. Thanks also to the many who refereed the manuscripts contained herein, and to North Carolina State University, the Naval Research Laboratory, and Texas Instruments for the resources which the organizers used before, during, and after the symposium.

F.J. Bartoli, Jr.
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April 1990

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PART I

Bulk Crystal Growth and Properties

GROWTH OF LARGE-DIAMETER CdZnTe AND CdTeSe BOULES FOR $Hg_{1-x}Cd_xTe$ EPITAXY: STATUS AND PROSPECTS

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ABSTRACT

Single crystals of CdTe or dilute alloys of $Cd_{1-y}Zn_yTe$ ($y \leq 0.04$) and $CdTe_{1-z}Se_z$ ($z \leq 0.04$) with low defect density and large single-crystal area (>30 cm^2) are required as substrates for high-quality epitaxial $Hg_{1-x}Cd_xTe$ thin films in the infrared (IR) detector industry. Bridgman or gradient freeze has been the most common current technique used for growing these materials. This paper reviews the current status and the evolution at SBRC of one variation of the Bridgman technique, viz., vertical-modified Bridgman (VMB), for producing large-area substrates with excellent uniformity and reproducibility. CdTe, $Cd_{1-y}Zn_yTe$ ($y \leq 0.04$) and $CdTe_{1-z}Se_z$ ($z \leq 0.04$) boules of 5- to 7.5-cm diameter have been grown unseeded in the present version of the VMB growth system. In general, under optimum growth conditions, the boules have the smallest grain structure (several grains) at the tip end with enhancement of grain selection as the cylindrical body of the boule is approached, resulting in one predominant and large grain occupying 70 to 80 percent of the entire boule volume; (111)-oriented $Cd_{1-y}Zn_yTe$ and $CdTe_{1-z}Se_z$ substrates with single-crystal areas as large as 50 to 60 cm^2 have been obtained from these boules. Crystal quality characterized by x-ray rocking curve, IR transmission (2.5 to 20 μm), low-temperature photoluminescence, and Hall-effect measurements as a function of temperature, showed a strong correlation with the starting material quality (especially that of elemental Te and Se). Analyses of the thermal history during growth reveals that the presence of the ampoule (with charge) increases the temperature inside the furnace by 10 to 15 degrees. The temperature gradient at the tip was measured to be 8 to 10°C/cm and it dropped to 4 to 5°C/cm beyond 2.5 cm from the tip – where rapid enhancement of grain selection takes place in most boules. The effect of this temperature rise on the initial crystallization near the tip of a boule can be explained from the numerical thermal model that was developed for the growth process with radiative and conductive heat transfer included and using a temperature profile similar to that existing in the actual growth furnace. Conditions for maximizing the fraction solidifying with a slightly convex interface, hence maximizing the single-crystal yield are discussed.

INTRODUCTION

Various growth methods have been applied in the past to the bulk growth of CdTe. This is mainly due to the difficulty of obtaining high quality single-crystal material of large size. In comparison with the highly developed group IV and III-V materials, there are several factors, viz., higher ionicity, reactivity and lower stacking fault energy in II-VI materials which in general make it more difficult for achieving large single crystals with low defects. Although different growth methods, viz., vapor phase growth, solution growth, and melt growth have all been used for growing bulk CdTe crystals, Bridgman and gradient freeze techniques of the melt growth process are the two most common current techniques used for growing large-diameter CdTe and dilute alloys of $Cd_{1-y}Zn_yTe$ ($y \leq 0.04$) and $CdTe_{1-z}Se_z$ ($z \leq 0.04$) boules.

The use of lattice-matched substrates for growth of $Hg_{1-x}Cd_xTe$ epitaxial layers has been shown to reduce the interfacial dislocation density and improve layer morphology. Both CdZnTe and CdTeSe have been used as substrates for the growth of HgCdTe by liquid-phase epitaxy (LPE) [1,2]. CdZnTe succeeded the binary compound CdTe several years ago because of greater hardness, lower dislocation density, and the advantage of lattice matching (resulting in fewer misfit dislocations at the substrate-layer interface). Recently, the growth of HgCdTe on lattice-matched substrates of CdTeSe by metal-organic chemical vapor deposition (MOCVD) has been reported [3], supporting the importance of close lattice matching for improved HgCdTe layer quality for MOCVD growth.

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Although alternative ("foreign") substrate materials, such as GaAs with an intervening CdTe buffer layer, have been used for the growth of HgCdTe by both MOCVD and molecular beam epitaxy (MBE), the lattice mismatch between HgCdTe and CdTe generates dislocations at the interface and can degrade the HgCdTe layer properties. Current investigation of the growth of lattice-matched CdZnTe layers grown on GaAs by MOCVD indicates promise of a possible replacement for bulk substrates of CdZnTe (and perhaps also CdTeSe) in the future. However, current development of next-generation hybrid infrared detector arrays relies upon active layers of HgCdTe grown by LPE, and the substrate materials required, at least at the present time, are in bulk crystal form with large single-crystal area (>30 cm^2) and low defect density.

It is expected from the phase diagrams of the two alloy systems (Cd-Zn-Te and Cd-Te-Se) that composition control can be maintained over longer boule lengths for CdTeSe than for CdZnTe, because the equilibrium distribution coefficient of CdSe is about 0.97 in CdTe compared with 1.31 for ZnTe in CdTe.

In this paper, results are reported of CdTeSe and CdZnTe boules ≥5 cm in diameter grown vertically and unseeded in a specially designed multiple-zone furnace assembly with a computerized control and monitoring system [4]. Parameters required for improved crystal quality based on growth experiments and numerical thermal model of the growth process are reviewed. Finally, factors influencing reproducibility of single crystal yield and quality are discussed.

CRYSTAL GROWTH AND EVALUATION

The crystal growth apparatus, optimum thermal conditions from thermal modeling of growth process, crystal growth procedure, and evaluation of grown crystal are described in this section.

Growth Apparatus

The crystal growth furnace assembly is shown schematically in Figure 1. The furnace can accommodate growth ampoule up to 7.5 cm in diameter. Temperature profiling of the furnace assembly was accomplished with a thermocouple array consisting of 11 thermocouple junctions 0.5 in. apart. The thermocouple array was positioned inside the middle furnace (melt or hot zone, Figure 1) to monitor temperature distribution both circumferentially and along the vertical axis (longitudinally). Temperature was displayed in real time on the video screen and all measured data were available for printout or storage on hard disk. Temperature profile data were obtained as a function of time with loaded ampoule in position, to monitor temperature distribution and fluctuations in temperature during the entire crystal growth period.

Thermal Modeling of Growth Process

From fundamental heat-transfer considerations it is known that for crystal growth from the melt in the vertical Bridgman configuration a slightly convex (toward the melt) liquid-solid interface is favorable for grain selection and helps to prevent spontaneous nucleation at the ampoule wall. Although the thermal conditions at the interface can be controlled to a large extent by furnace design features and furnace parameters, the thermal properties of the charge will have a major influence on the interface shape and position. The most important of the thermal properties of the charge is its thermal conductivity. While the magnitude of the thermal conductivity influences the thermal coupling between the furnace and the charge, a difference in thermal conductivity values for the solid crystal and the melt at the interface can lead to unfavorable interface shape (i.e., concave toward the melt).

Thermal diffusivity (α), which is related to the thermal conductivity (k) by $k = \alpha\rho C_p$, where ρ and C_p are density and specific heat (at constant pressure), respectively, was measured for both solid and liquid CdTe and $Cd_{0.96}Zn_{0.04}Te$. Results of the thermal diffusivity measurements [4] as a function of temperature for both CdTe and CdZnTe, showed only a 20% increase in