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PREPARATION AND CHARACTERIZATION OF INFRARED MATERIALS.(U)
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: AFOSR-TR-80-0414	2. GOVT ACCESSION NO.: AD-A084324	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): PREPARATION AND CHARACTERIZATION OF INFRARED MATERIALS.	5. TYPE OF REPORT & PERIOD COVERED: Final: 1/1/77-12/31/79
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): August F. Witt	8. CONTRACT OR GRANT NUMBER(s): AFOSR-77-3202
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Dept. of Materials Science & Engineering, Room 13-4134, MIT, Cambridge, Mass. 02139	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 2306/C2, 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS: AFOSR/NE, Bolling AFB, DC 20332	12. REPORT DATE: Apr[redacted]80
	13. NUMBER OF PAGES: 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release. Distribution Unlimited.

Final rept. 1 Jan 77-31 Dec 79

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

2306

DTIC ELECTE MAY 19 1980 A

18. SUPPLEMENTARY NOTES

C2

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Infrared materials, Indium Antimonide, dopant segregation, compositional modulation, Czochralski crystal growth

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

The research was concerned with advancing Bridgman and Czochralski crystal growth for the preparation of infrared materials. The program focused on the growth of macro-superlattices in InSb for the preparation of SFRL matrices.

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Unclassified

AFOSR-TR- 80-0414

TO: AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Final Technical Report

Grant AFOSR-77-3202

Period 1/1/79 - 12/31/79

PREPARATION AND CHARACTERIZATION OF INFRARED MATERIALS

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RESEARCH OBJECTIVES

The primary objectives of this research program were:

(A) In broad terms: (1) to advance the established processing techniques for growth of IR materials; (2) to improve crystalline perfection and composition control achievable in single crystals to beyond the state of the art.

(B) In specific terms: (1) growth of n-type InSb single crystals with uncontrolled microsegregation variations reduced to less than 10%; (2) growth of heavily doped (Bi) InSb single crystals with optimized composition control; (3) growth of InSb macro-superlattices, suitable for spin-flip Raman laser structures.

ACCOMPLISHMENTS

<u>Czochralski Growth</u>: Through the installation of a co-axial sodium heat-pipe in the hot-zone it was possible to virtually eliminate radially asymmetric heat input to the charge and to reduce periodic growth rate variations during rotational pulling by in excess of one order of magnitude ($\frac{\Delta R}{R}$ from 0.65 to 0.05). Through appropriate vertical positioning of the charge container within the heat pipe, the radius of curvature of non-faceted crystal-melt interfaces could be increased by a factor of 4 (from 2 cm to 8 cm). With the decreased radial thermal gradient in the melt, crystals could be grown in which the growth interface facet comprised in excess of 90% of the crystal-melt boundary (the growth interface could be maintained planar, with $r = \infty$, over 90% of its area). The relative instability of the growth system brought about by the decreased radial and axial thermal gradients associated with the heat pipe installation could be eliminated through the installation of a conical Ni-reflector, located co-axially about the growing crystal at a distance of about 1 cm from the melt surface. This conical reflector, inclined by 45° to the horizontal, reduced significantly the view factor of

the growing crystal and by screening IR radiation from the melt surface and heat-pipe led to a pronounced increase in the thermal gradient along the crystal. It was thus possible (1) to reduce power consumption during growth, (2) to decrease the destabilizing vertical thermal gradient in the melt and thus segregation controlling melt convection and (3) to increase significantly the maximum possible rate of crystal pulling. In an extension of this research program, we are investigating the applicability of the modified growth technique to liquid encapsulation growth at temperatures up to 1200°C. Temperature control and temperature stability of the hot-zone was studied under both constant flux conditions (control T/C at the heat-pipe) and constant temperature conditions (control T/C buried at the bottom of the charge container). It was found that constant temperature conditions provided for a more stable melt temperature and could compensate for Joule heating effects associated with extended current pulsing during the formation of macro-superlattices in InSb.

Bridgman-Stockbarger Growth: One of the primary deficiencies of crystal growth by the Bridgman technique was identified as inadequate heat transfer control and associated non-planarity of the crystal-melt interface. On the basis of heat transfer calculations, it was concluded that effective heat flow control across a growth interface can be established by replacing a conventional tube furnace with differentially operated co-axial heat pipes separated by a variable distance. This arrangement provides for two isothermal regions connected by an adiabatic thermal gradient region in which the freezing melt interface can be localized. By using an adiabatic zone confined by several coaxial low conductivity metal tubes (separated by Zircar insulation) it could be shown that parallel heat flow is maintained over a distance of up to 2 cm, providing for planar solidification isotherms over a ΔT of more than 100°C.

Composition Control During Czochralski Growth: Applying a heat pipe to Czochralski growth it was found that for impurities with $k_o > 5 \times 10^{-3}$ rotation induced axial composition variations ($\frac{\Delta C}{C}$) can be reduced from 0.38 to 0.011 and radial segregation variations from 0.29 to 0.02. Associated with the decrease of the radial thermal gradient in the hot-zone is a pronounced expansion of the growth interface facet (111) which exhibits no measurable radial composition gradient. In an extension of this research program, the effect of possible evaporative dopant loss from the melt surface on radial segregation is being investigated. This study makes use of liquid encapsulation ($PbO - B_2O_3$) to prevent evaporative loss. Also under investigation is the effect of encapuslation on the temperature distribution in the melt and on the related micro- and macrosegregation behavior.

Crystal Perfection Associated with Czochralski Growth: A conspicuous side-effect of thermal gradient reduction in modified Czochralski growth is the pronounced tendency for twinning. An exhaustive analysis indicated that two factors contribute primarily to the relative lattice instability, extended growth interface facet formation to the periphery of the growing crystal and low axial thermal gradients along the crystal. A conical Ni-reflector located co-axially about the growing crystal was found to provide the gradient control required and resulted in a marked reduction of twinning in InSb. A detailed analysis of line and point defect formation in InSb and Ge is being undertaken as an extension of this program.

Growth of Heavily Doped (Bi) InSb: Growth of InSb containing in excess of 1 mole% BiSb by the Bridgman technique was studied. It was found that excessive curvature of the solidification istherm and the associated non-planarity of the growth interface contribute primarily to radial compositional non-uniformity and instability of the gorwing crystal. In a conventional Bridgman-

Stockbarger configuration, the results published in the open literature could be duplicated but could not be improved upon. Data obtained served as a basis for the design of a growth configuration (described above) in which it is expected to achieve control over the growth interface morphology and to eliminate the stability controlling radial segregation effect.

Growth of InSb Macro-Superlattices Suitable for Spin-Flip Raman Laser Structures: The specified basic materials requirement for a tunable SFRL InSb matrix consists of a periodically modulated free carrier concentration with $\frac{\Delta C}{C} \gtrsim 2$; further constraints include: monotonic layer width change of less than 1% over 60 layers, random layer thickness variations < 10%, dopant layer thickness in the range from 10 to 30 μm, radius of curvature of layers > 5 cm, base free carrier concentration of $< 5 \times 10^{15}/cm^3$ at 77°K. The growth of the desired structure was approached stepwise. Dopant modulation at the desired level was accomplished by current pulsing at a density of 25 A/cm^2. Growth interface morphology control, increase of its radius of curvature to in excess of 8 cm could be achieved by both extended facet growth as well as by reducing the radial thermal gradient in the melt through lowering the charge appropriately into the heat pipe cavity. The primary obstacles to realizing functional SFRL structures of InSb are (1) pronounced twinning tendency at the required minimized radial thermal gradient in the melt and (2) anomalous and as yet unexplained facet growth and segregation behavior associated with pulsing at high current densities. Comparative analyses with the growth behavior with other III-V compounds, particularly with InP, suggested that the low thermal gradient along the growing crystal, the result of reducing the radial thermal gradient, contributes significantly to twin formation. To overcome this deficiency a conical thermal reflector was installed co-axially about the crystal at about 1 cm above the melt surface. Growth experiments in this configuration at pulling rates up to 3"/h yielded single crystal free of twin formation. (The thermal configuration developed is currently applied to liquid encapsulation growth of InP.) The anomalous facet growth and segregation behavior of InSb with current pulsing is still subject of extensive study. The anomaly consists of a significant attenuation of enhanced current induced dopant incorporation from the periphery. Morover, upon etching the facet growth region in InSb reveals a planar defect which increases in density markedly with current application. The defects appear exclusively on facet with each covering an area of 30 to 80% of the total faceted area. Positive identification and efforts for its elimination are currently pursued..

Research Interactions with Other Groups and Agencies: The research program has over its two year duration been fully coordinated with the research efforts on spin-flip Raman lasers by Professor P. Wolff of the Research Laboratory for Electronics (RLE) at MIT. In view of the rather promising results of modulated segregation in InSb, the cooperative research effort is being continued.

The principle investigator has been able to make extensive use of the research results and the insight gained into advanced IR materials processing from this program in two National Materials Advisory Board Panels concerned with processing of Si and HgCdTe as IR-type electronic materials.

Research on Bridgman-type growth of Bi-doped InSb within this program established the basis for a new approach to growth in confined geometry and provided significant input to the on-going efforts on growth of HgCdTe by the National Aeronautics and Space Administration. Czochralski growth, making use of advanced heat pipe technology and of IR-reflectors for thermal gradient control, as developed in this two year research program is currently being adopted for growth of InP and GaAs by liquid encapsulation. Efforts are also underway to apply thermal reflectors to growth of Si.

PUBLICATIONS

1. The Application of a Heat-Pipe to Czochralski Growth, E. Martin, A. F. Witt and J. R. Carruthers, J. Electrochem. Soc. 126, 284 (1979).

2. Growth of Heavily Bi-Doped InSb by the Czochralski Technique, P. Tissier and A. F. Witt (to be submitted to the J. Electrochem. Soc.).

3. On the Use of IR-Reflectors for Thermal Gradient Control During Czochralski Growth, A. F. Witt (to be submitted to J. Crystal Growth).

4. Anomalous Facet Growth and Segregation Associated with Current Controlled Growth in Doped InSb, M. Wargo, A. F..Witt (in preparation for J. Electrochem. Soc.).

PROFESSIONAL PERSONNEL ASSOCIATED WITH THE RESEARCH EFFORT

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THESES

E. P. Martin, (Ph.D.), "Convection and Segregation Phenomena in Low Prandtl Number Melt Growth Systems: A Quantitative Experimental and Numerical Approach", 1977.

P. Tissier, (M.S.), "Growth and Characterization of Heavily Doped InSb for Infra-Red Applications", 1979.

M. J. Wargo, (Ph.D., not completed as yet), "Fluid Dynamic Effects on Segregation During Liquid-Solid Phase Transformations".