

REPORT DOCUMENTATION PAGE

AD-A220 444

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT

Approved for public release;
distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

ARO 22916.15-EL-A

6a. NAME OF PERFORMING ORGANIZATION
Dept. of Physics
University of Maryland6b. OFFICE SYMBOL
(If applicable)

7a. NAME OF MONITORING ORGANIZATION

U. S. Army Research Office

6c. ADDRESS (City, State, and ZIP Code)

College Park, Maryland 20742-4111

7b. ADDRESS (City, State, and ZIP Code)

P. O. Box 12211
Research Triangle Park, NC 27709-22118a. NAME OF FUNDING/SPONSORING
ORGANIZATION

U. S. Army Research Office

8b. OFFICE SYMBOL
(If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

DAAG-29-85-K-0052

8c. ADDRESS (City, State, and ZIP Code)

P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NO.PROJECT
NO.TASK
NO.WORK UNIT
ACCESSION NO.

11. TITLE (Include Security Classification)

Diluted Magnetic Semiconductors (unclassified)

12. PERSONAL AUTHOR(S)

Anderson, James R.

13a. TYPE OF REPORT

Final

13b. TIME COVERED

FROM 85/4/1 TO 89/12/31

14. DATE OF REPORT (Year, Month, Day)

90/3/26

15. PAGE COUNT

6

16. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COTATION CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Diluted Magnetic Semiconductors, Magnetization, Exchange, Magnetotransport, Solid State Recrystallization, $Hg_{1-x}Mn_xTe$, Cadmium, INORGANIC CHEMISTRY. (TJG)

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

Growth and physical properties of diluted magnetic semiconductors (DMS) were investigated. Growth included Bridgman, solid state recrystallization, and liquid phase epitaxy of $Hg_{1-x}Mn_xTe$ and $Hg_{1-x-y}Mn_xCd_yTe$. Very uniform crystals were produced by solid state recrystallization. Physical properties studied included magnetization, optical response, and magnetotransport. From magnetization, the exchange interactions among magnetic ions have been deduced. Modulated spectroscopy gave details of the electronic structure of DMS and the quality of the material was indicated by the line widths. Magnetotransport, carried out in some cases to 30 T, showed a large negative magnetoresistance and subsequent increase. The $Hg_{1-x-y}Mn_xCd_yTe$ has considerable promise for avalanche photodiodes between 1.2 and 1.8 μm micrometers.

20. DISTRIBUTION/AVAILABILITY STATEMENT

☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL

Final Report

Diluted Magnetic Semiconductors

Grant Number: DAAG29-85-K-0052

Author of Report: J.R. Anderson

Name of Institution: University of Maryland, College Park, Maryland

1. Forward

Diluted magnetic semiconducting (DMS) systems are compound semiconducting systems composed of cations from columns II or IV of the Periodic Table of the Elements and anions from column VI. The term magnetic refers to the fact that some of the cations are replaced by magnetic ions such as manganese, cobalt, iron, gadolinium, or europium. These systems provide an opportunity to investigate the confluence of semiconductor physics and magnetism in a single system. That is, the semiconducting properties are influenced strongly by a magnetic field and the semiconducting carriers contribute to the magnetic features. A summary of some of these properties has been given by Furdyna.¹

In the present report we describe our investigations of the responses of DMS systems to magnetic fields, light, and electric fields.

2. Report

A. Statement of the Problem Studied

This report summarizes our investigations of methods of growth and of physical properties of DMS systems. The aim of our studies was to learn how the magnetic and semiconducting properties of DMS systems are related so that the potential of these materials for application can be realized. To accomplish this we investigated Bridgman, solid-state-recrystallization, and liquid-phase-epitaxy growth.

magnetization, magnetotransport, and modulated reflectance. Our studies suggest that magnetic-field modulation may be used to enhance the device capabilities of these materials.

B. Summary of Most Important Results

Our most important results are summarized as follows:

1. A recipe for Bridgman growth of $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ was developed; single crystals with mobilities comparable to those of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ with the same energy gap have been obtained. Calibration curves making use of the ratios of the x-ray line intensities, $\text{CdL}\alpha/\text{TeL}\alpha$ and $\text{MnK}\alpha/\text{TeL}\alpha$, from electron microprobe energy dispersive analysis, have been obtained for determination of the x-values in both $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$.²
2. Solid-state recrystallization growth of $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ produced high-quality single crystal boules of length 7 cm in which the variation of x over the central 4 cm was less than 5%. Defect densities have been estimated from transport measurements. For example, for $\text{Hg}_{0.875}\text{Mn}_{0.125}\text{Te}$ the room temperature electron concentration was about $2 \times 10^{16} \text{cm}^{-3}$, a value consistent with estimates of the intrinsic density at the room temperature band gap (230 meV). At low temperatures the samples became p-type and magnetic boilloff was observed.³ Some crystals were converted to n-type by annealing in Hg vapor.
3. In collaboration with Dr. S.H. Shin of the Rockwell Science Center $\text{Hg}_{1-x-y}\text{Mn}_x\text{Cd}_y\text{Te}$ crystals were grown by liquid phase epitaxy and the electronic structures studied by electrolyte electroreflectance and magnetotransport. This quaternary system has been developed as a promising candidate for avalanche photodiodes at wavelengths between 1.2 and 1.8 μm .^{4,5} In particular, by appropriate choices of x and y, resonance structures have been obtained at 1.55 μm . This work has been summarized in our patent on avalanche photodiodes.⁶
4. A new technique, *mobility spectrum analysis* (MSA) employs a combination of the low-field Hall signal and magnetoresistance to obtain the carrier concentration as a continuous function of mobility. As a result, we are able, without

additional assumptions, to extract the maximum amount of information from the data concerning the types of carriers contributing to the conductance and their mobilities. This approach has been shown to work well for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and HgTe , materials for which the energy bands are not influenced significantly by a magnetic field.^{7,8} Up to now, however, the MSA technique has not been successful for DMS systems because a magnetic field has a strong influence on the electronic structure, but work on this problem is continuing.

5. Magnetization studies of both II-VI and IV-VI DMS systems have shown that the dominant contributions to the magnetization are single magnetic ions and magnetic ion pairs. We have developed a model to obtain the exchange parameters for these DMS materials from a combination of high-field magnetization and low field susceptibility studies.^{9,10,11,12}
6. Photorefectance has the potential to be very important for characterization of semiconducting systems because no electrical contacts are needed and the technique is nondestructive. We have developed an extremely successful double modulation experimental technique for photorefectance. In addition, following the work of Aspnes and Froya,¹³ we have derived a model that takes account of the spatial variation of the internal electric field at surfaces and interfaces and fits both the exciton structure and the Franz-Keldysh oscillations. Consequently we believe photorefectance now has a fundamental basis like electroreflectance and can be applied systematically as a semiconductor characterization tool.¹⁴
7. Anodization studies supplemented by surface Raman scattering are in progress. We have shown that the surface-enhanced Raman effect is a powerful tool for examining the reaction products produced during oxidation/reduction cycles at the surface of a DMS system such as $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$.

C. Publications and Technical Reports

1. Magnetization of $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$, J.R. Anderson, M. Gorska, L.J. Azevedo, and E.L. Venturini, *Phys. Rev.* 33, 4706 (1986).
2. Large Negative Magnetoresistance of $\text{Cd}_{9/10}\text{Mn}_{1/10}\text{Se}$, J.R. Anderson, W.B. Johnson, and J.K. Furdyna, *Jour. Phys. Chem. Solids* 48, 481 (1987).
3. Phase Differences of Quantum Oscillations of the Hall Voltage, R.G. Mani and J.R. Anderson, in *High Magnetic Fields in Semiconductor Physics*, Springer Series in Solid-State Sciences, ed. G. Landwehr (Springer-Verlag, Berlin, 1987) Vol. 71, p. 436.
4. Determination of Electrical Transport Properties Using a Novel Magnetic Field-Dependent Hall Technique, W.A. Beck and J.R. Anderson, *Jour. Appl. Phys.*, 62, 541 (1987).
5. Phase Differences between Quantum Oscillations of the Magnetoresistance and Hall Effect in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, R.G. Mani, J.R. Anderson, and W.B. Johnson, *Jour. Phys. Chem. Solids* 48, 687 (1987).
6. Magnetization and Susceptibility of $\text{Pb}_{1-x}\text{Nm}_x\text{Se}$, M. Gorska and J.R. Anderson, *Solid State Communications* 63, 1055 (1987).
7. Inversion Asymmetry in $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$, J.A. Nobel, J.R. Anderson, and W.B. Johnson, *Phys. Rev.* B36, 6012 (1987).
8. The Magnetophonon Effect in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, R.G. Mani, J.R. Anderson, J.B. Choi, and D.A. Nelson, *Phys. Rev.* B36, 9146 (1987).
9. Magnetic Properties of $\text{Pb}_{1-x}\text{Gd}_x\text{Te}$, M. Gorska, J.R. Anderson, and Z. Golacki, *Mat. Res. Soc. Symp. Proc.* Vol. 89, 1987 Materials Research Society, p. 119.
10. $\text{Hg}_{1-x}\text{Mn}_x\text{Cd}_y\text{Te}$ Alloys for 1.3-1.8 μm Photodiode Applications, S.H. Shin, J.R. Anderson, W.E. Tennant, M. Gorska, C.R. Lu, and M. Fotouhi, *Mat. Res. Soc. Symp. Proc.* Vol. 89, 1987 Materials Research Society, p. 267.
11. Analysis of Multiband Conduction in HgTe by Magnetic-Field Dependent Hall Techniques, W.A. Beck, F. Crowne, J.R. Anderson, M. Gorska, and Z. Dzuiba, *J. Vac. Sci. Technol.* A6, 2772 (1988).
12. Influence of the Resonant Acceptor State on the Magnetotransport Properties of Zero-Gap $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$, R.G. Mani and J.R. Anderson, *Phys. Rev.* 38, 3354 (1988).
13. Magnetic Susceptibility and Exchange in IV-VI Diluted Magnetic Semiconductors, M. Gorska and J.R. Anderson, *Phys. Rev.* B38, 9120 (1988).
14. Magnetic Susceptibility of PbTe and PbSe , M. Gorska and J.R. Anderson, *Acta Physica Polonica* A75, 273 (1989).
15. Shubnikov de Haas Oscillations in HgTe/CdTe Superlattices Grown by Laser Molecular-Beam Epitaxy, Lamya Ghenim, R.G. Mani, J.R. Anderson, and J.T. Cheung, *Phys. Rev. Rapid Communications* B39, 1419 (1989).
16. Magneto transport on HgTe/CdTe Superlattices, Lamya Ghenim, R. Mani, J.R. Anderson, and J.T. Cheung, *High Magnetic Fields in Semiconductor Physics II*, Springer Series in Solid State Sciences, Vol. 87, p. 207 (1989).

17. The Shallow Resonant Acceptor in Semimagnetic, Zero-gap $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$, R.G. Mani and J.R. Anderson, Inst. Phys. Conf. Ser. No. 95: p. 371 (1989).
18. Crystal Growth of $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ by Solid State Recrystallization, R.G. Mani, T. McNair, C.R. Lu, and R. Grober, Jour. Crystal Growth 97, 617 (1989).
19. High-Field Magnetization of IV-VI Diluted Magnetic Semiconductors, J.R. Anderson, G. Kido, Y. Nishina, and M. Gorska, Phys. Rev. B41, 1014 (1990).
20. High-Field Magnetization of IV-VI Diluted Magnetic Semiconductors, J.R. Anderson, G. Kido, Y. Nishina, and M. Gorska, Semicond. Sci. Technol. 4 - to be published.
21. Quantum Interference Effects and Weak Localization in HgTe/CdTe Superlattices Grown by Laser Molecular Beam Epitaxy, L. Ghenim, R. Mani, J.R. Anderson, and J. Cheung, Semicond. Sci. Technol. 4 - to be published.
22. Electrolyte Electroreflectance of LPE-Grown $\text{Hg}_{1-x-y}\text{Mn}_x\text{Cd}_y\text{Te}$, C.R. Lu, J.R. Anderson, M. Gorska, and S. Shin, Solid State Communications - to be published.
23. HgMnCdTe Avalanche Photodiode, Soo H. Shin, J.R. Anderson, and John G. Pasko, United States Patent, Patent Number 4,862,236; 29 August 1989.

D. Participating Scientific Personnel and Advanced Degrees Earned

R.G. Mani	Ph.D.
M.M. Gorska	
C.R. Lu	Ph.D.
D. Streett	
L. Ghenim	
T. McNair	
J.A. Nobel	Ph.D.
W.A. Beck	Ph.D.

3. Bibliography

1. J.K. Furdyna, J. Appl. Phys. 64, R29 (1988).
2. J.R. Anderson, M. Gorska, L.J. Azevedo, and E.L. Venturini, Phys. Rev. 33, 4706 (1986).
3. R.G. Mani, T. McNair, C.R. Lu, and R. Grober, Jour. Crystal Growth 97, 617 (1989).
4. S.H. Shin, J.R. Anderson, W.E. Tennant, M. Gorska, and C.R. Lu, Mat. Res. Soc. Symp. Proc. Vol. 89, 1987 Materials Research Society, p. 267.
5. C.R. Lu, J.R. Anderson, M. Gorska, and S. Shin, Solid State Communications - to be published.
6. Soo H. Shin, J.R. Anderson, and John G. Pasko, U.S. Patent, Patent No. 4,862,236; 29 August 1989.
7. W.A. Beck and J.R. Anderson, Jour. Appl. Phys. 62, 541 (1987).

8. W.A. Beck, F. Crowne, J.R. Anderson, M. Gorska, and Z. Dzuiba, J. Vac. Sci. Technol. A6, 2772 (1988).
9. M. Gorska and J.R. Anderson, Solid State Commun. 63, 1055 (1987).
10. M. Gorska, J.R. Anderson, and Z. Golacki, Mat. Res. Soc. Symp. Proc. Vol. 89, 1987 Materials Research Society, p. 119.
11. M. Gorska and J.R. Anderson, Phys. Rev. B38, 9120 (1988).
12. J.R. Anderson, G. Kido, Y. Nishina, and M. Gorska, Phys. Rev. B41, 1014 (1990).
13. D.E. Aspnes and A. Froya, Solid State Commun. 7, 155 (1969).
14. C.R. Lu, J.R. Anderson, M. Fotouhi, and T.F. Kuech, Effect of the Nonuniform Internal Electric Field in MBE-Grown GaAs on the Photorefectance Line Shape - submitted to Phys. Rev.