CONSORTIUM MEETINGS ON SUBMICRON HETEROSTRUCTURES OF DILUTED MAGNETIC SEMICONDUCTORS (U)
Purdue Univ Lafayette in 1987 N00014-86-K-0706

UNCLASSIFIED
The Principal Investigators along with their co-investigators are continuing to maintain high visibility in the area of II-VI semiconductors and their heterostructures with special emphasis and focus on the diluted magnetic semiconductors (DMS's). The enclosed list of publications during 1986-1987 documents the high level of activity and the interactive climate which prevails in the Consortium. The enclosed list of invited talks, seminars and colloquia, and contributed talks shows that the semiconductor community continues to have intense interest in the area of focus of the Consortium.

During 1986-1987 the DARPA/URI on Submicron Heterostructures of Diluted Magnetic Semiconductors convened three meetings of the Principal Investigators, Members of the Advisory Panel and Drs. J.D. Murphy and Kristl Hathaway.

1. DARPA/URI Consortium Meeting
   Boston, Massachusetts
   December 3, 1986

2. DARPA II-VI MATERIALS & PROCESSING CONFERENCE
   Washington, DC
   April 7-9, 1987

3. Fall Meeting of the DARPA/URI Consortium
   Purdue University, W. Lafayette, IN
   November 4-6, 1987

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(I) Growth of DMS heterostructures and their device potential

(a) MBE growth of DMS films and multilayered structures
(Schetzina/Cook)

Considerable progress has been made at North Carolina State University (NCSU) in the development of photoassisted molecular beam epitaxy. A number of CdTe and CdMnTe films doped with In have been grown and studied. Mobilities as large as 2500 cm²/(V-s) have been obtained for CdTe films at low temperatures. Reproducible carrier concentrations ranging from 6x10¹⁵ to 7x10¹⁷ cm⁻³ have been obtained by systematic variation of the In oven temperature. P-type CdTe:Sb films have been successfully prepared with room temperature hole concentrations of 3x10¹⁸ cm⁻³ and hole mobilities of 81 cm²/(V-s).

Double-crystal x-ray diffraction studies indicate that the doped CdTe epilayers have a high degree of structural perfection. X-ray rocking curves as narrow as FWHM(400)=18 arc sec have been obtained for CdTe:In films grown on (100) CdTe substrates. This FWHM is comparable to the best ever obtained for CdTe epilayers grown by any technique.

The successful doping of CdTe films chemically compatible and closely lattice matched with HgCdTe, may provide the basis for a planar monolithic device technology featuring integration of HgCdTe focal plane arrays with on-board signal processing based on CdTe devices. In connection with the development of such a technology, a number of mask sets for photolithography have been developed at NCSU which define Schottky diodes, p-n junction diodes, field effect transistors, bipolar transistors, tunnel structures, charge coupled devices for signal readout of focal plane arrays, photodiode-transistor amplifier circuits and other masks for specialized optoelectric devices.

At NCSU, CdTe MESFET devices have been recently fabricated and tested. Depletion-mode FET structures with 5µm and 100µm gate lengths showed excellent Schottky diode characteristics, with some diode structures displaying reverse breakdown voltages as large as 14V.
(b) Pseudomorphic ZnSe/GaAs MISFET Devices
(Gunshor/Kolodziejski/Melloch/Otsuka and co-workers)

ZnSe (a zincblende semiconductor with a room temperature bandgap of 2.7 ev) is used as the insulator in a working GaAs MISFET device. A coherent, dislocation-free ZnSe/GaAs heterointerface has been obtained via the molecular beam epitaxy (MBE) of pseudomorphic ZnSe onto "as-grown" GaAs MBE epilayers. The small (0.25%) lattice constant mismatch between ZnSe and GaAs allows for the growth of 1000Å insulating layers devoid of strain-relieving misfit dislocations. Dramatic differences are seen in the nucleation of ZnSe onto MBE-grown GaAs epilayers compared to typical use of bulk GaAs substrates. Nucleation of ZnSe onto bulk substrates occurs as three-dimensional islands coalesce to form the insulating layer, whereas nucleation on MBE-grown epilayers results in a layer-by-layer growth. High resolution transmission electron microscopy examining the interfacial region of the pseudomorphic ZnSe/GaAs epilayer heterojunction confirms the existence of the coherent interface such that the lattice constant in the plane of the layers is the same for the two materials. Having the capability of achieving a nearly perfect epitaxial interface has allowed for the fabrication of a GaAs MISFET devices. MIS capacitors were used to determine the n-channel thickness and doping. The I-V characteristics of the MISFET devices were measured at room temperature and 77K. This II-VI/III-V heteroepitaxial interface has all the potential of the AlGaAs/GaAs structure with the additional advantage of larger band discontinuities.

(c) DMS based LED and injection laser heterostructures
(P. Becla, Francis Bitter National Magnet Laboratory, MIT)

Infrared LED and injection laser heterostructures of HgMnTe and HgCdTe have been fabricated. Spontaneous emission from the LED's with peak at 5.3μm has been observed upto 140K in the pulsed mode and 90K in the CW mode. Stimulated emission with threshold current density of \(-1200\) A/cm² (pulsed) has been observed at 5.4μm from laser heterostructures at 77K.
(II) Growth of bulk and layer structures of DMS's

The Atomic Layer Epitaxy (ALE) system has been ordered (Furdyna-Notre Dame); it is expected to be "on the air" by mid-November 1987. The new MBE facility at Purdue (Gunshor/Kolodziejski) is now operational and superlattices are being fabricated. The MBE facilities at NCSU (Schetzina) is producing a variety of doped and undoped epilayers and superlattices. The Purdue Central Crystal Preparation Facility (Furdyna/Ramdas/Debska) supplies highly purified elements to the MBE facilities at Purdue and NCSU. Growth of bulk DMS continues at Purdue (Debska), Francis Bitter National Magnet Laboratory (Becla) and NCSU (Bachmann). Insulator growth studies of DMS material (Lucovsky) are being initiated; preliminary studies of SiO$_2$ growth on CdTe wafers by remote plasma-assisted CVD are just now getting underway. Furdyna and Debska have succeeded in preparing DMS ternary alloys based on Co (e.g. Cd$_{1-x}$Co$_x$Se). This significantly expands the scope of DMS's.

(III) Instrumentation for physical investigation/characterization

(a) Transmission electron microscope
(N. Otsuka)

The installation of a JEM 2000 EX high resolution electron microscope has been completed. A point resolution, 2.5Å, has been obtained with the standard pole piece of the objective lens (spherical aberration coefficient $C_s$: 1.4 mm). By November 1987, this pole piece will be replaced by an ultra-high resolution pole piece ($C_s$: 0.7 mm) which is expected to give a point resolution, 2.1Å.

(b) Electrical characterization of MBE films
(Gunshor/Reifenberger)
The electrical characterization of the MBE films grown at Purdue by Professors Gunshor and Kolodziejski is underway in Reifenberger's laboratory. A new high impedance electrometer system has been developed that permits the rapid and accurate measurement of the resistivity and Hall coefficient of the wide band-gap materials. Measurements spanning a wide range of temperatures will be possible in the near future.

(c) Scanning Tunneling Microscope
(Dow and co-workers)

The STM at Notre Dame is operational. It has been tested on gold and graphite, providing routinely images with resolution below 10Å. Work on the reduction of noise and increase in resolution is in progress.

(d) Fourier transform spectrometer
(Ramdas)

The spectrometer manufactured by BOMEM has been delivered to Purdue (Ramdas). The spectrometer currently capable of a maximum resolution of 0.002 cm\(^{-1}\) and a spectral coverage 5-10,000 cm\(^{-1}\), has been installed. Work on exit optics to accommodate absorption and reflectivity measurements and entrance optics to enable photoluminescence is in progress.

(IV) Physical investigations

(a) Spin-flip Raman scattering from Cd\(_{1-x}\)Mn\(_x\)Te:In epilayers and modulation doped Cd\(_{1-x}\)Mn\(_x\)Te:In/CdTe superlattices grown by photo-assisted molecular beam epitaxy
(Ramdas/Schetzina and co-workers)
The observation of the 's-d' exchange interaction enhanced spin-flip Raman shift from electrons in Cd$_{1-x}$Mn$_x$Te:In epilayers and modulation doped Cd$_{1-x}$Mn$_x$Te:In/CdTe superlattices is studied to demonstrate successful, controlled doping during the growth by photoassisted molecular beam epitaxy. Resonance Raman enhancement; confinement of electrons to the CdTe wells in the superlattices; the penetration of the electronic wave functions into the Cd$_{1-x}$Mn$_x$Te barriers; the spatial location of the intentionally introduced donors, the strength of the 's-d' interactions; these are the issues addressed in the experiments.

(b) Photoluminescence and excitation spectroscopy

(i) Doped epilayers and superlattices (Schetzina)

Extensive low temperature photoluminescence and excitation luminescence experiments have been completed. On the basis of these measurements along with variable-temperature Hall effect data, the ionization energy of In donors in CdTe films has been determined to be 14.8±0.2 meV. From an analysis of the luminescence data for CdTe:Sb films, the ionization energy of Sb acceptors is estimated to be 65±2 meV.

(ii) Bandoffsets in the CdTe/(Cd,Mn)Te heterostructures (Nurmikko/Gunshor/Kolodziejski)

Magneto-optical studies have been carried out in order to pin down the question of bandoffsets in (100) oriented CdTe/(Cd,Mn)Te quantum wells. This information is critical in the design of future electro-optical devices based on this heterostructure. The experimental work includes the use of photoluminescence excitation spectroscopy and Resonant Raman spectroscopy to make careful measurements of lowest confined particle excitonic transitions in a CdTe quantum well. It is found that in order to accurately determine the small valence band
offset, it is imperative to account properly for the exciton Coulomb interaction in this unusual case of a quasi-2D electron and and quasi-3D hole. A variational theory has been developed which extends the treatment of excitons beyond the usual case of good confinement for both quasi-particles. As a consequence it is determined that the valence band offset is mainly determined by the lattice mismatch strain extrapolating to zero (within 10 meV) is the ideal limit of a strain free structure.

(iii) Influence of electric fields on excitons in ZnSe/(Zn,Mn)Se Quantum Wells
(Nurmikko/Gunshor/Kolodziejski)

Nurmikko and co-workers have applied sizable electric fields, at values above the classical field ionization threshold for excitons in bulk ZnSe, to demonstrate substantial Stark effects in the recombination spectra of a ZnSe/(Zn,Mn)Se quantum well. The measured shifts have been correlated with theory which successfully considers the added influence of the electron-hole Coulomb field on the net electric field in the structure. Furthermore, in a multiple quantum well structure grown on a n+ GaAs substrate, proper choice in the polarity of the applied field can inject hot electrons into the adjacent wide gap structure. They have demonstrated this by observing the yellow electroluminescence from the Mn-ion d-electron transition at the (Zn,Mn)Se layers of the superlattice, excited by the hot electrons emitted from the GaAs substrate.

(iv) P- and As- doped CdMnTe
(Becla/Schetzina and co-workers)

Photoluminescence and infrared absorption studies on P- and As- doped CdMnTe clearly show acceptor bound magnetic polarons (BMP's) whose energies are fitted using self-consistent numerical calculations. At liquid helium temperatures the acceptor-BMP's have total magnetic moments as large as 120 Bohr magnetons.
(c) Non-linear optical effects in DMS's
(Wolff/Yuen/Schetzina/Cook and co-workers)

A large value of \(5 \times 10^{-4}\) for third-order nonlinear susceptibility \(\chi^{(3)}\) with response time in the picosecond range has been measured at 10.6 \(\mu\)m in HgTe and HgMnTe at \(\sim 300\) K. This is attributed to interband population modulation. It does not saturate below 1 MW/cm\(^2\).

Resonance scattering levels in the conduction band of HgCdSe:Fe have shown to yield large values for \(\chi^{(3)}\) due to the energy dependence of the scattering mechanism. Further enhancement of \(\chi^{(3)}\) can be obtained if the resonance scattering level lies closer to the Fermi energy.

Narrow bandgap (50-250 meV) HgMnTe shows strongly nonlinear current-voltage (I-V) characteristics. Bulk samples display a negative differential resistivity that can be attributed to thermal causes. However, pulsed current studies on epilayer samples indicate that there is a nonlinear component due to an electronic effect. The study of the I-V curves as a function of magnetic field will shed light on the acceptors binding energy in these materials.

(d) \(sp-d\) and \(d-d\) exchange interaction in DMS's.

(i) \(Ab initio\) theory of \(sp-d\) and \(d-d\) exchange interaction in DMS's
(Ehrenreich and co-workers)

An \(ab initio\) theory for the \(sp-d\) and \(d-d\) exchange interactions of CdMnTe was completed and found to be in good agreement with experiment. The calculation includes the realistic band structure. The implementation of the superexchange formalism is believed to be as good as the best that has been previously given for other materials. A simple model has been constructed using these results, which permits accurate estimates of exchange parameters in other DMS. The chemical trends observed so far have been accurately predicted.

The anisotropic superexchange (Dzyaloshinski-Moriya interaction) is being calculated using the same formalism as above, but including spin-orbit interactions. The results are being used to interpret the EPR experimental linewidths
observed by Furdyna's group.

(ii) **Raman scattering from antiferromagnetically coupled Mn$^{2+}$ pairs in Cd$_{1-x}$Mn$_x$S and Cd$_{1-x}$Mn$_x$Se**

(Rodriguez/Ramdas/Aggarwal)

Isolated pairs of antiferromagnetically coupled magnetic ions possess a series of energy levels whose separation is determined by the nearest-neighbor exchange constant $J_{NN}$. We report Raman transitions between these energy levels in Cd$_{1-x}$Mn$_x$S and Cd$_{1-x}$Mn$_x$Se. At the lowest temperatures, the ground to first excited state transition is observed and allows direct measurement of $J_{NN}/k_B$: $-10.6 \pm 0.2$ K in Cd$_{1-x}$Mn$_x$S and $-8.1 \pm 0.2$ K in Cd$_{1-x}$Mn$_x$Se. Transitions to higher excited states occur at higher temperatures.

(iii) **Low-temperature magnetization**

(Shapira/Aggarwal/Becla/Furdyna/Heiman)

The low temperature magnetization of DMS's exhibits steps at high magnetic fields. The steps are due to energy level crossing for pairs of nearest-neighbor Mn spins. The steps yield the Mn-Mn exchange constant and the concentration of pairs in the crystal. During the last year we have studied the magnetization steps in Hg$_{1-x}$Mn$_x$Te and Cd$_{1-x}$Mn$_x$Te. The latter study complements the study of the magnetization steps by spin-flip Raman scattering.

(iv) **Bound magnetic polaron.**

(Isaacs/Heiman/Furdyna and co-workers)

Large bound magnetic polaron energies have been observed in CdMnSe using inelastic light scattering from donor spin-flip transitions to temperatures as low as 0.4 K. Spin-flip transitions to fields of 30 T show magnetization steps in CdMnTe
(3 steps) and CdMnSe (2 steps).

(v) Stannite DMS's
(Shapira/Wolff and co-workers)

Mean-field calculations show that ordered-alloy DMS have enhanced magnetic properties: 5 times for linear chains of Mn and 30 times for stannite-type Mn ordering.

Studies of II-VI DMS have shown that the antiferromagnetic interaction is mainly due to interactions between nearest-neighbor Mn spins. The wurtz-stannite structure of compounds like Cu$_2$Zn$_{1-x}$Mn$_x$GeS$_4$ is similar to the wurtzite and zinc-blende structures of the II-VI DMS's, but in this structure the Mn ions are never nearest-neighbor cations. It was therefore suggested by Wolff and Ram-Mohan that the antiferromagnetic interaction in this structure will be reduced substantially relative to that in the analogous II-VI materials. This suggestion has been confirmed experimentally in measurements of the susceptibility and magnetization of CVT-grown single crystals of Cu$_2$Zn$_{1-x}$Mn$_x$GeS$_4$.

(vi) Temporal response of Mn$^{2+}$ spin system in DMS's
(Furdyna and co-workers)

Furdyna and co-workers have discovered that the temporal response of the exchange-coupled Mn$^{2+}$ spin system in Cd$_{1-x}$Mn$_x$Te significantly speeded up by addition of a small atomic fraction of Fe into the system. This response should be of considerable interest in the application of DMS's in fast magneto-optical devices.
(e) Faraday Effect in DMS's

(Ehrenreich)

The magneto-optical figure of merit for DMS is being examined and compared with that of other materials such as YIG. For the infra-red range appropriate for CdMnTe (~0.62μm), the DMS are probably the best candidate materials for isolators and modulators, in agreement with the assessment of Gunshor and collaborators. A complementary examination of the promise of IR Detectors involving the new high-Tc superconducting materials is currently in its beginning stages.

(f) Structural studies

(i) Twinning and dislocations

(Furdyna and co-workers)

A systematic program of structural studies of DMS, including the study of twinning and dislocations, has been launched. In addition to providing basic structural knowledge, this program will help in evaluating ternary and quaternary substrate candidates for epitaxy applications.

(ii) Exotic DMS's: their band structure

(Dow/Newman and co-workers)

Kathie Newman and associates have shown that Hg₄Mn₄Te, for x=0.5, can have a chalcopyrite structure with a band gap approximately half that of the random alloy. They are now determining the stability of new ordered phases of alloys A_{IV}B_{IV}C_{VI} having either cubic or hexagonal symmetry, using cluster variation methods. A local-density theory of MnTe has been worked out, and differs in its results from those of Zunger, supporting work by Ehrenreich.
(g) Electrostatic and magnetostatic modes in semiconductor superlattices
(Rodriguez and co-workers)

The propagation of acoustic phonons, optical phonons or of magnetostatic modes in the interface between two elastic, dielectric or magnetic media presents many phenomena of great physical interest. One of the simplest forms of interface modes is that consisting of waves traveling parallel to the interface and decaying exponentially into the adjoining media. A well known example is that of surface plasmons. The recent growing interest in superlattices has led to investigations of surface modes in these structures. A study was made of spin wave excitations propagating along the layers of superlattice and possessing the ordinary Bloch periodicity along the axis. The dispersion formula of such modes was obtained and applied to the antiferromagnetic state of superlattices formed by diluted magnetic semiconductors.
PUBLICATIONS
(1986-87)


13. R.L. Aggarwal, S.N. Jasperson, P. Becla and J.K. Furdyna, "Optical Determination of the Antiferromagnetic Exchange Constant Between Nearest-Neighbor Mn$^{2+}$ ions in Zn$_{0.95}$Mn$_{0.05}$Te", Phys. Rev. B 34, 5894 (1986).


70. N. Otsuka, Y.E. Ihm, K.A. Harris, J.W. Cook, Jr. and J.F. Schetzina, "Transmission Electron Microscope Study of Hg-Based Multilayer


92. K.C. Hass and D. Vanderbilt, "Structural Properties of II-VI Crystals and Alloys", Proceedings of the 18th Int. Conf. on Physics of Semiconductors,


129. Y. Shapira and N.F. Oliveira, Jr., "High-Field Magnetization Steps and the Nearest-Neighbor Exchange Constant in Cd_{1-x}Mn_xSe, Cd_{1-x}Mn_xTe and Zn_{1-x}Mn_xSe", Phys. Rev. B 35, 6888 (1987).


131. Kebede Beshah, David Zamir, Piotr Becla, Peter A. Wolff and Robert G. Griffin, "Te and Cd NMR Study of Local Structure and Bonding in


168. C.S. Lent, M.A. Bowen, J.D. Dow, R.S. Allgaier, O.F. Sankey and E.S. Ho, "Relativistic Empirical Tight-binding Theory of the Energy Bands of GeTe, SnTe, PbTe, PbSe, PbS and Their Alloys", Superlattices and Microstructures 2, 491-499 (1986).

169. C.S. Lent, M.A. Bowen, R.S. Allgaier, J.D. Dow, O.F. Sankey and E.S. Ho, "Impurity Levels in PbTe and Pb$_{1-x}$Sn$_x$Te, Solid State Commun. 61, 83-7 (1987).

170. R.V. Kasowski, M.-H. Tsai and J.D. Dow, "Dependence on Ionicity of the (110) Surface Relaxations of Zincblende Semiconductors" (submitted).


175. G. Kim, J.D. Dow and S. Lee, "Theory of Charge-state Splitting of Deep Levels Associated with Sulfur Pairs in Si" (submitted).


180. M.-H. Tsai, R.V. Kasowski and J.D. Dow, "Relaxation of the non-polar (10\bar{1}0) Surface of Wurtzite AlN and ZnS", Solid State Commun. 64, 231-3 (1987).


182. D.W. Jenkins, R.-D. Hong and J.D. Dow, "Band Structure of InN", Superlattices and Microstructures (in press).


INVITED TALKS, COLLOQUIA, SEMINARS AND CONTRIBUTED TALKS

(1986-87)


*2. J.K. Furdyna, "Optical Device Applications of Diluted Magnetic Semiconductors", Int. Conf. of the Society for Optical Engineering (SPIE), April 7-18, 1986, Innsbruck, Austria.


* Invited


42. S. Rodriguez, "Raman Scattering in Diluted Magnetic Semiconductors", Seminar presented in the School of Physics, Pontificia Universidad Catolica de Chile, Santiago, Chile, Oct. 10, 1986.


83. H. Ehrenreich et al., "Bond Relaxation in Hg1-xCdTe and Related Alloys", Workshop on the Physics and Chemistry of Mercury Cadmium Telluride,
Dallas, TX, Oct. 7-9, 1986.


97. A. Barrientos, C. Almasan, T. Datta, E.R. Jones, Jr., R.N. Bicknell and J.F. Schetzina, "Low Temperature dc Susceptibility of Cd\textsubscript{1-x}Mn\textsubscript{x}Te Bulk, Thin Films and Thin Film Superlattices", BAPS 31, 252 (1986).


100. S. Hwang, K.A. Harris, Y. Lansari, D.K. Blanks, J.W. Cook, Jr. and J.F. Schetzina, "Optical and Electrical Properties of Hg\textsubscript{1-x}Cd\textsubscript{x}Te Films and HgTe-CdTe Superlattices Grown by Molecular Beam Epitaxy", BAPS 31, 655 (1986).


104. M. Dobrowolska, Z. Yang, H. Luo, J.K. Furdyna, K.A. Harris, J.W. Cook, Jr. and J.F. Schetzina, "Far-Infrared Magneto-Absorption in HgTe/CdTe and Hg\textsubscript{1-x}Mn\textsubscript{x}Te/HgTe Superlattices", 1986 U.S. Workshop on MCT, Dallas, TX (1986).


106. H. Luo, M. Dobrowolska, Z. Yang, J.K. Furdyna, K.A. Harris, J.W. Cook, Jr. and J.F. Schetzina, "Far-Infrared Magnetospectroscopy of HgTe and
Hg$_{1-x}$Mn$_x$Te Monolayers Grown by MBE", 1986 U.S. Workshop on MCT, Dallas, TX (1986).


*119. J.F. Schetzina, "Dilute Magnetic Semiconductor Quantum Wells", Seminar at Purdue University, Physics Department, West Lafayette, IN (1986).

*120. J.F. Schetzina, "Properties of II-VI Quantum Well Structures Grown by MBE", Seminar at University of Notre Dame, Physics Department, South Bend, IN (1986).


*125. A.V. Nurmikko, presentation at Bell Communications Research and Bell Labs, January 1986.

*126. A.V. Nurmikko, presentation at International School of Semiconductor Physics, Jasowicz, Poland, April 1986.


*129. A.V. Nurmikko, presentation at Technical University of Helsinki, Finland, July 1986.

*130. A.V. Nurmikko, presentation at University of Tampere, Finland, August 1986.


150. A.V. Nurmikko, presentation at Modulated Semiconductor Structures, Montpellier, France, July 1987 (3 papers).


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