# REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified

1b. RESTRICTIVE MARKINGS:

2a. SECURITY CLASSIFICATION AUTHORITY

2b. D

AD-A283 120

3. DISTRIBUTION / AVAILABILITY OF REPORT: Approved for public release; Distribution unlimited

4. PEI

5. MONITORING ORGANIZATION REPORT NUMBER(S)

DTIC ELECTE AUG 10 1994 D

6a. NAME OF PERFORMING ORGANIZATION: Research Fdn. of State Univ. of NY on behalf of SUNY at Buffalo

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code): P.O. Box 9, Albany, New York

7b. ADDRESS (City, State, and ZIP Code): 800 N. Quincy St., Arlington, VA 22217-5000

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-86-K-0730

8c. ADDRESS (City, State, and ZIP Code): 800 N. Quincy St., Arlington, VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

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

11. TITLE (Include Security Classification): Laser-induced effects in solids

12. PERSONAL AUTHOR(S): Bruce McCombe

13a. TYPE OF REPORT: Final

13b. TIME COVERED: FROM 6/1/86 TO 12/31/90

14. DATE OF REPORT (Year, Month, Day): 12/31/90

94-25185

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

| FIELD | GROUP | SUB-GROUP |
|---|---|---|
| | | |
| | | |

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

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


This project is directed at the experimental investigation of novel semiconductor materials and quantum-confined structures, as well as model biological membranes, with the overall goal of exploiting the unique high power, tunability , and availability in "difficult" regions of the spectrum of Free Electron Lasers (FELs) to explore and determine the applicability of novel properties and phenomena in these systems.

In-house optical facilities spanning the spectral region from the visible and near ultra violet (UV) through the far infrared (FIR), as well as the FIR FEL facility at the University of California Santa Barbara are used to investigate the electronic states and optical and magneto-optical response of the wide gap diluted magnetic semiconductor ZnFeSe, quantum wells and superlattice structures fabricated in GaAs/AlGaAs and the strained-layer system InGaAs/AlGaAs. In addition, the novel properties of model biological membranes are explored.


20. DISTRIBUTION / AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION: Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL: Bruce D. McCombe

22b. TELEPHONE (Include Area Code): (716) 636-2017

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

94 8 09 078

LASER-INDUCED EFFECTS IN SOLIDS

Contract #N0001486K0730

June 1, 1986 - December 31, 1990

P. I. : B. D. McCombe

Department of Physics and Astronomy
SUNY at Buffalo
Buffalo, N.Y. 14260



FINAL REPORT

## I. General and Specific Objectives

This project is directed at the experimental investigation of novel semiconductor materials and quantum-confined structures, as well as model biological membranes, with the overall goal of exploiting the unique high power, tunability , and availability in "difficult" regions of the spectrum of Free Electron Lasers (FELs) to explore and determine the applicability of novel properties and phenomena in these systems.

In-house optical facilities spanning the spectral region from the visible and near ultra violet (UV) through the far infrared (FIR), as well as the FIR FEL facility at the University of California Santa Barbara are used to investigate the electronic states and optical and magneto-optical response of the wide gap diluted magnetic semiconductor ZnFeSe, quantum wells and superlattice structures fabricated in GaAs/AlGaAs and the strained-layer system InGaAs/AlGaAs. In addition, the novel properties of model biological membranes are explored.

## II. Facilities/Instrumentation.

Several optical facilites were established at SUNY at Buffalo under a previous grant to complement and expand existing capabilities, and to provide necessary experimental tools to perform preliminary experiments prior to carrying out measurements at FEL facilities. These include an optically-pumped submillimeter laser, a flashlamp-pumped dye laser, a Krypton-ion laser, and a He-Cd laser. In addition, various accessories and detectors were purchased and set-up to expand existing spectroscopic capabilities. The following spectroscopic equipment is available for these studies, in addition to the lasers mentioned above: a BOMEM DA-03 Fourier Transform Infrared Spectrometer; a SPECAC polarizing Fourier Transform Interferometer; two argon-ion lasers; a dye-laser; SPEX 1401 and 1403 double monochromators with cooled photomultiplier detectors, and a SPEX 1681B single monochromator with PbS and InSb detectors. Two superconducting magnet systems, 9T and 8T, are also used for these investigations.

## III. Findings/Progress

Progress over the past 18 months is summarized below by individual project. Since the work on model biological membranes showed rather little promise for exploitation with FELs, it was phased out during this period.

A. <u>Optical and Magneto-optical Studies of ZnFeSe and ZnSe/ZnFeSe Quantum Wells</u>

The so-called Diluted Magnetic Semiconductors combine both magnetic and semiconducting properties which have a number of interesting optical and magneto-optical applications. Much effort has gone into narrow gap and intermediate gap materials containing manganese, but much less attention has been focussed on wider gap materials containing iron. Reflectance and magnetoreflectance studies have been carried out on ZnFeSe layers and on ZnSe/ZnFeSe single quantum wells with widths between 100 A and 200 A (Fe concentration of 10%) grown by molecular beam epitaxy(MBE). For the quantum wells the heavy hole exciton features were observed to split into two circularly polarized components. The two components exhibit markedly asymmetrical behavior as a function of magnetic field. The right circular polarized component shows a magnetic red shift, while the left circular polarized component shows a blue shift up to 2T and then saturates. This behavior can be qualitatively understood as follows: The magnetic-field-induced splitting of the heavy holes inside the ZnFeSe layers overcomes the zero field valence band offset at a relatively modest value of applied magnetic field. The $m_J = -3/2$ holes become localized in the ZnFeSe layers, while the $m_J = 3/2$ holes remain in the ZnSe layers. In the conduction band the electrons remain localized in the ZnSe layers at all values of applied magnetic field. This leads to so-called type-I behavior (electrons and holes localized in the same layer) for the right circularly polarized and type-II behavior (electrons and holes localized in adjacent layers) for the left circularly polarized components of the heavy hole excitons. The strong asymmetry of the splitting in a magnetic field associated with the spin segregation of holes provides a measure of the valence band offset in this diluted magnetic semiconductor system. These interesting magnetic field dependent segregation effects may provide the basis for interesting magneto-optical properties which can be varied by additional optical pumping with high power lasers.

B. Optical Pumping Effects in Multiple-Quantum-Well Structures in the Presence of External Electric Fields

Electric fields applied to semiconductor quantum wells through the fabrication of p-i-n structures with multiple quantum wells(MQWs) forming the "i" region provide the possibility of creating and tailoring large optical nonlinearities. In the presence of strong optical excitation the electronic structure of the confined states can be changed in a controllable way. An interband reflectivity study has been carried out on GaAs/AlGaAs multiple quantum wells in a p-i-n structure. The MQWs are sandwiched between heavily doped p-type AlGaAs and heavily doped n-type GaAs layers. The GaAs quantum wells in the "i" layer are lightly doped with Si donors over the central 1/3. Several lines from Ar-ion and Kr-ion lasers spanning photon energies from above the AlGaAs band gap to slightly above the confinement gap of the GaAs wells have been used to pump these structures over a range of pump intensities. At zero pump intensity the reflectivity spectra show multiple features in the region of the ground state confinement energy as well as the excited confinement states. The numerous lines are attributed to variation of the electric field throughout the MQW structure due to depletion in the wells with a concomitant variation in the confinement subband energies in different wells. In the presence of a pump laser beam the features shift to higher energy at varying rates such that at high excitation intensities the features tend to merge together toward several discrete lines corresponding to the ground and excited confinement states of these QWs in the absence of an electric field. These results are similar to the behavior of the reflectivity features in the presence of increasing forward bias with no laser pump which confirms the interpretation. In the presence of optical pumping the photogenerated electron-hole pairs are spatially separated in the rather wide wells (240A and 450A); this produces a dipolar screening field that opposes the built-in electric field tending to flatten out the potential and approaching the limit of a uniform set of identical square quantum wells at high enough excitation intensities. This provides the same qualitative effect as forward bias. Low intensity photoluminescence(PL) experiments were also performed in the presence of external bias and provide additional clarification of the above interpretation.

These large photoinduced effects show promise in applications as modulators and other nonlinear elements. FELs provide the necessary high intensity and tunability to investigate these structures in detail.

### C. Delocalized Electronic States and Charge transfer Processes in GaAs/AlAs Quantum Wells

In GaAs/AlAs quantum wells with thin GaAs layers (< 40A) the energy of the n = 1 conduction band confinement subband, $E_1^c$ , lies above the lowest AlAs conduction band minimum (at the X-point of the Brillouin zone). In this case the lowest electronic states are in the AlAs layers, while the corresponding highest -lying hole states are confined in the GaAs wells, and the structure becomes a so-called type-II superlattice. In quantum wells with GaAs layer thickness approximately 100A the $E_2^c$ confinement subband in the GaAs is approximately degenerate with the AlAs conduction band minimum at the X-point. In this case the electrons of energy $E_2^c$ are delocalized and can move freely throughout the structure.

We have investigated two such GaAs/AlAs quantum-well structures with L(GaAs) = 100A and 140A and L(AlAs) = 75A. The delocalization of the n = 2 electrons manifests itself in a variety of optical experiments. Below, we briefly discuss three such experiments. (a) Magnetoreflectance spectroscopy shows that the binding energy of the $E_{2h}$ exciton associated with the n = 2 delocalized electronic states is much smaller than the calculated value. The calculation, on the other hand agrees quite well with experimental data for the ground state $E_{1h}$ exciton. No disagreement was found for the $E_{2h}$ exciton in the GaAs/AlAs structure with L(GaAs) = 140A, for which the $E_2^c$ state lies below the AlAs X-point conduction band. In the 100A wells the electron of the $E_{2h}$ exciton is delocalized while the hole remains confined inside the GaAs wells. As a result, the electron-hole Coulomb interaction is reduced compared with the case where both electron and hole are localized in the same layers, and thus the exciton binding energy is reduced correspondingly. (b) Raman spectra recorded with the laser photon energy resonant with the $E_{2h}$ exciton contain features corresponding to longitudinal-optical phonons in <u>both</u> the GaAs (290 $cm^{-1}$) and the AlAs (400 $cm^{-1}$) layers. This is direct evidence that the electrons with energy near $E_2^c$ are not localized in the GaAs wells, but are also found with a finite probability in the AlAs layers as well. When the laser photons are not resonant with the $E_{2h}$ exciton, the Raman spectra contain <u>only</u> the GaAs longitudinal-optical phonon features. (c) Photoluminescence excitation experiments on a GaAs/AlAs MQW structure with 18 100A wells and one 130A well show clear evidence of charge transfer from the 100A wells to the single wider well via the $E_2^c$ delocalized states.

These experiments indicate the possibility of using such structures for infrared detectors. Additional work with tunable high intensity sources on appropriately designed samples is required to verify the interpretation and model, and to determine the feasibility of possible applications.

D. <u>Saturation Spectroscopy of Holes and Confined Impurities in MQW Structures</u>

High power far infrared lasers enable the study of nonlinear optical phenomena in this difficult region of the spectrum. Included in this class of experiments are saturation of cyclotron resonance and impurity resonance transitions in semiconductors. Saturation spectroscopy in the presence of a magnetic field yields information on the dynamics of carriers that are either bound to impurities or free in Landau levels.

The FEL at the University of California at Santa Barbara has been used to study the saturation of the absorption due to: (a) Cyclotron resonance(CR) of free holes in a <111>-oriented InGaAs/GaAs strained-layer superlattice; and (b) the ground state to first excited state transition in a magnetic field of shallow donor impurities doped in the barriers of GaAs/AlGaAs quantum wells.

Magnetotransimission measurements were carried out on these samples for various power levels ranging from 500 $mW/cm^2$ to 1.25 $kW/cm^2$. Laser lines at 164 microns and 200 microns wavelength were used. In the strained-layer sample (a) saturation of the CR begins at 1.5 $W/cm^2$. The Landau level momentum relaxation time obtained from the CR linewidth was found to be approximately 5 picoseconds for power levels less than 1 $W/cm^2$ reducing to 1.2 picoseconds for 1.25 $kW/cm^2$. The decrease may be due to the increased role of carrier-carrier scattering at high powers. Fitting of the saturation behavior to obtain the Landau level lifetime is in progress. The non-parabolicity of the valence band in this sample (non-uniform spacing of the Landau levels) in addition to permitting the saturation of CR is also manifested in other ways. For example, a shift of the CR position to higher magnetic fields with increasing laser power along with an increased linewidth at the highest laser powers that is not amenable to explanation based on a simple two level model. This behavior reflects that fact that the higher-lying hole Landau levels are closer together than the lowest pair.

Saturation of the impurity ground state to first excited state resonance for donor impurities confined in quantum wells has been observed for the first time in the sample described in (b) above. Detailed analysis is presently being carried out.

E. <u>Electric Field Effects in <111>-Oriented InGaAS/AlGaAS Strained-Layer Superlattices</u>

Strain-induced electric fields have been predicted to occur in <111>-oriented strained-layer superlattices having the zinc-blende crystal structure. These large electric fields lead to interesting nonlinear optical properties both in the region of the band gap of the constituent materials as well as in the region of the confinement subband energies (the infrared to far infrared). We have carried out far infrared magnetotransmission (cyclotron resonance) and near infrared reflectivity, magnetoreflectivity, and photoluminescence studies of several <111>- and <100>-oriented InGaAs/AlGaAs strained-layer superlattices. Nominal well and barrier thicknesses were 70A and 140A, respectively, for all samples. Indium content was approximately 10%, and Al content in the barriers ranged from 0 to 20%. Hole cyclotron resonance was observed in the <111>-oriented samples as verified by circular polarization studies. In the sample with GaAs barriers an anti-crossing behavior attributed to subband-Landau level crossing was observed when the magnetic field was tilted away from the normal to the sample surface. This gives a value of 11 meV for the energy separation of the lowest two "heavy-hole" subbands. No anticrossing behavior was observed in the sample with 20% Al in the barriers due to the larger effective mass and larger subband separation in this case. A doublet structure was observed in the interband reflectivity spectra for the sample with GaAs barriers; the separation between features in the doublets was also 11 meV. The existence of the doublets is due to breaking of the parity selection rule; thus these results are taken to be direct evidence for the existence of large built-in electric fields in these structures. Attempts to modify the electric fields by optical pumping with CW lasers have not been successful. Much higher powers are required to study the screening effects and the optical nonlinearities.

## IV. Future Plans

- Continue saturation spectroscopy studies with the Santa Barbara FEL.
- Initiate high intensity laser studies of screening and nonlinearities in the strained layer superlattice systems and in semiconductor quantum wells in large electric fields produced in p-i-n structures; NIST FEL.
- Carry out detailed investigation of resonant delocalization effects in GaAs/AlAs superlattices and possible applications; investigate effect of electric fields produce by strong optical pumping in type-II short period GaAs/AlAs superlattices.
- Initiate high intensity laser studies of tailored quantum wells in the 10 micron region. Study effects of modulation doping and nonlinearities in this spectral region.
- Continue exploration of novel magneto-optical properties of Diluted Magnetic Semiconductors. Initiate studies of optical nonlinearities associated with the intra-ion transitions of Fe in the Fe-based DMS.

## V. Personnel

Dr. Bruce D. McCombe, P.I.
Dr. Athos Petrou, co-P.I.
Dr. John Ho, co-P.I.

Dr. Radha Ranganathan, Postdoctoral Research Associate

Mr. X. Liu, Research Project Assistant
Mr. Y. J. Wang, Research Project Assistant(partial support)
Mr. B. S. Yoo, " " " " "
Mr. W. J. Li, " " " " "
Ms. R. Qiu, " " " " "

## VI. Funding

Funds received: 1988............$125,000
1989............$125,000