

USE OF ELECTROREFLECTANCE TO CHARACTERIZE
MATERIALS WITH A VIEW OF PREDICT DEVICE PERFORMANCE

FINAL REPORT

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INTRODUCTION AND DESCRIPTION OF WORK PERFORMED

The optical study of semiconductor surfaces, heterojunctions, multiple quantum wells and superlattices under electromodulation has received increasing attention and has given many valuable results in recent years. Outside our group, most of these studies have employed photoreflectance (PR) and have been limited to III-V medium-band-gap systems. Our work under DARPA sponsorship, until shortly before the beginning of this contract, has been devoted primarily to the study of narrow-band-gap materials, in particular mercury cadmium telluride, and has utilized almost solely electrolyte electroreflectance (EER) measurements performed in the vicinity of the E_1 and $E_1 + \Delta_1$ transition energies. However, in the year preceding the onset of this contract, in response to perceived national needs the focus of our work shifted to an investigation of those properties of (1) heavily doped wide-band-gap II-VI materials and heterojunctions and (ii) superlattices and multiple quantum wells (MQW's) which are most important in determining the performance of advanced devices, in particular optoelectronic devices.

The work performed under this DARPA contract is largely an extension of the most recent work begun under DARPA contract #N00014-87-K-0296 and in the final year of DARPA contract #N0014-86-K-0070. It was motivated by both fundamental scientific and applied reasons. From a fundamental point of view, superlattices, MQW's and wide-band-gap II-VI heterojunctions were on the frontier of semiconductor research and remain there, as is evidenced by the heavy Japanese investment in their investigation. From an applied point of view, the payoff for the growth of the correct high-quality wide-band-gap heterostructures includes the solid-state blue laser, which is needed for military applications such as space and underwater communication and for civilian applications such as laser writing for high-density memory devices and for fiber-optic communications. We also initiated and completed under this contract a very accurate determination of the band gap of lattice-matched GaAs/GaInP MQW's and superlattices. Those structures have emerged as an important alternative to the GaAs/GaAlAs system for application to many microwave devices.

The experimental work performed under this contract consisted primarily of EER, but also included spectroscopic ellipsometry (SE), PR and Raman measurements, as well as vacuum electroreflectance, a new type of electroreflectance (ER) measurement developed in the

Microphysics Laboratory under DARPA contract #N00014-86-K-0070 and improved under this contract. EER contains several advantages for the characterization of semiconductor structures such as those which we have investigated:

(1) EER spectra, like PR and other ER spectra, are very sharp. This allows the spectra to be fit well using a much simpler lineshape with fewer adjustable parameters than is the case for SE, reflectance or even thermoreflectance data. In turn, this allows the accurate determination of transition energies, lineshapes and other physically meaningful fitting parameters.

(2) EER spectra, like PR and other ER spectra, are extremely sensitive to transitions between quantified well states and superlattice subband states, even revealing first-order forbidden transitions clearly. This is because the energy of such transitions is especially sensitive to an applied electric field. For the same reason they are even more sensitive to transitions between states localized on opposite sides of any interface, despite the small matrix elements for such transitions. This property of ER spectra is particularly important for the investigations undertaken under this contract because it allowed us to measure band offsets and even band profiles directly without relying on assumed simple models, as is necessary in determining band offsets from electrical measurements.

(3) EER allows one to study spectra as a function of bias and of applied modulating field or voltage. This possibility, which is not present for PR and is difficult to implement for VER, is essential for identifying with certainty the origin of important spectral features in the spectra arising from heterojunctions, MQW's and superlattices.

(4) Except for samples with semi-insulating substrates, EER yields reproducible data with an excellent signal-to-noise ratio.

(5) The theory of ER is well developed, at least for the low-field case, with that of EER being more fully developed than that of either PR or VER. This allows us to maximize the physical information available from a given low-field spectrum.

Howèver, despite these advantages, several problems remained in the use of EER. The most commonly known problems are experimental and result from the very nature of EER, which prohibits low-temperature measurements and in-situ measurements, can make high-temperature measurements difficult and allows the possibility of surface degradation by the electrolyte under the action of an external electric field, at least for some semiconductors. Because of these problems

with EER, most other investigators have abandoned EER in favor of PR, which does not suffer from these particular shortcomings. However, because PR does not share with EER the essential advantage (3) listed above, we have been able to use PR only sparingly, usually only to confirm our EER results. In contrast, from the perspective of the immediate goals of this contract, the experimental problems associated with EER were very minor.

The one serious problem which we encountered with the use of EER was of a very different nature; it was the lack of any satisfactory theory to use in the interpretation of ER or PR data on samples having built-in electric fields which are neither small nor uniform. ER and PR spectra obtained from samples having intermediate or large, nonuniform, built-in electric fields due to high doping levels or due to interdiffusion, as in ZnSe/GaAs and ZnSe/AlAs, displayed E_0 and $E_0 + \Delta_0$ lineshapes which were qualitatively different from the lineshapes observed at E_1 and Δ_1 , which were in agreement with the existing low-field theory. They were even more different from the lineshapes obtained from samples having intermediate or large, but uniform, built-in fields, which display many oscillations above E_0 . The E_0 lineshapes which we observed on heavily doped samples and on ZnSe/GaAs and ZnSe/AlAs heterojunctions were greatly broadened toward the high-energy side but did not display the oscillations characteristic of ER spectra obtained from samples having intermediate or large, but uniform, built-in fields.

In order to partially circumvent this problem, we measured the E_0 lineshape for a series of GaAs samples with known and increasing doping levels from $3 \times 10^{16} \text{ cm}^{-3}$ up to $3 \times 10^{18} \text{ cm}^{-3}$. This showed that the line shape depends rather sensitively on the doping level, with the asymmetric broadening increasing smoothly with increasing doping level, i.e., with increasing maximum (or average) built-in field. By using simple theoretical arguments for the effect of changes in the effective mass, we were then able to scale the GaAs results to ZnSe, and thus to determine the ZnSe built-in field, as well as to determine the GaAs and AlAs values of E_0 and to estimate the maximum built-in field in the GaAs and AlAs. However, the theoretical arguments used were of a simple semiclassical nature, and, even more importantly, the band and electric-field profiles on either side of an interdiffused II-VI/III-V heterojunction differ qualitatively from the corresponding profiles of a doped bulk semiconductor. Thus, in the absence of a quantitative theory, the values of the built-in fields and hence the magnitudes and diffusion lengths of the built-in diffusion could only be estimated from our EER data.

For this reason, and because of a similar problem encountered earlier when studying the effect of hydrogenation on GaAs/GaAlAs resonant tunneling structures, we launched a major effort to develop a quantitative theory for the E_0 and $E_0 + \Delta_0$ ER lineshapes of samples having large nonuniform built-in fields. We succeeded in developing a theory which could be used to obtain precise values of E_0 , $E_0 + \Delta_0$ and built-in field magnitudes for any given shape of a band profile or field profile. Although there existed no other reliable direct measurement with which to test the accuracy of the theory for other cases, the theory was found to give perfect agreement with other independent measurements for heavily doped GaAs. The theory allowed us to determine the range and magnitude of the interdiffusion in the ZnSe/GaAs and ZnSe/AlAs samples which we studied by EER. Thus, in one sense, the theory was very successful. However, the theory has substantial drawbacks. First, it has several more variable parameters than the low-field theory -- all of the low-field parameters plus the correlation length and any parameters required to describe the electric-field profile. Second, despite our best efforts, we have been unable to cast the theory in a form which does not require extremely intensive quantum-mechanical numerical computations for each effective mass and each field-profile functional form for which one wishes to fit ER data.

In order to fully understand the significance of the rich and unusual EER spectra obtained on the M E grown ZnSe/GaAs and ZnSe/AlAs heterojunctions which we studied, it was necessary to use those spectra to construct band profiles. Only in that way could we understand the relationship between our data and the electrical data gathered on the same samples by M.A. Haase and coworkers at the 3M corporation, who had given us the samples for study. Using conventional simple model band profiles, our data appeared to be completely inconsistent with theirs.

The development of the new theory of ER valid for built-in fields $E_{bi} \geq 5 \times 10^4$ V/cm, discussed above, was necessary in order to obtain accurate band profiles, but was not sufficient. The large built-in fields which we determined from that theory could arise only from substantial interdiffusion of Zn and Ga, and the existence of those fields was confirmed by the observation of crossover transitions from the ZnSe to a series of triangular-well states on the GaAs and AlAs side of the interfaces. Thus, although interdiffusion had not previously been suspected, we were forced to construct a three-parameter interdiffusion model having as parameters the amount of interdiffusion and the diffusion parameters on each side of the interface. Using that model we derived a functional form for the band profiles as a function of five physical parameters -- the three

parameters of the interdiffusion model, the band offset and the surface pinning energy of the ZnSe epilayers. Then, we constructed a program which calculated all of the observed transition energies as well as the measured maximum built-in fields as a function of those five parameters. Finally, we constructed a program which fit the transition energies and built-in fields as a function of the five physical parameters in order to find their values, which were overdetermined by our data. This new type of analysis finally yielded the sought after band profiles. It turned out that the band profiles we determined, although very different from those originally assumed by M. A. Haase, et al, to explain their electrical data, were equally consistent with that data.

In addition to our EER studies of ZnSe/GaAs and ZnSe/AlAs heterojunctions, both SE and Raman measurements were also performed. The SE measurements were used to confirm the EER values for the critical-point energies of ZnSe, GaAs and AlAs away from the interface. The Raman measurements first involved building a new experimental setup, mostly from the remains of an old abandoned Raman setup. They were much more extensive than the SE measurements. They were used for three primary purposes: (1) to provide an independent measure of the electric field at the interface in the GaAs or AlAs, (2) to study the quality of the ZnSe epilayers, and (3) to search for any evidence of the existence of Zn_3As_2 or Ga_2Se_3 islands near the interface, or any other islands, as had been seen in some heterojunctions grown by other techniques.

The second major investigation conducted under this contract was a measurement of the band offsets of lattice matched GaAs/Ga_{0.51}In_{0.49}P MQW's and superlattices by EER. This investigation, which was performed entirely under this contract, was made possible by the loan of several samples of outstanding quality grown by M. Razeghi. Systems containing GaAs/GaAlAs heterojunctions have emerged as promising for optoelectronic and microwave devices. However, these systems have exhibited some practical problems for use in devices, such as the formation of DX centers in the GaAlAs and the tendency of Al to oxidise in lasing material. Lattice-matched GaAs/GaInP systems do not suffer from those problems and thus were emerging as a potentially superior candidate for use in microwave devices such as HEMT's, HT's, HIGFET's and p-channel HEMT's, and in optical devices such as lasers, solar cells, photodiodes and infrared detectors. Neither the band offsets nor the intraband, intersubband optical-transition energies had been directly measured before. Our investigation provided the first reliable, accurate values for those important quantities, the knowledge of which is necessary for device design.

Both of these two major projects involved repeated EER data runs to ensure reproducibility as well as to improve the statistical reliability of the data, and involved massive theoretical and computational efforts. In addition to those projects, we also investigated the surface field in moderately Si doped n-type LEC GaAs before and after surface doping with H_2 . We compared our EER measurements in the vicinity of the E_0 and $E_0 + \Delta_0$ critical points with 77 K internal photoemission (IPE) data obtained by C. Coluzza, et al. from Pd Schottky-barrier structures grown on the GaAs. We observed the strengths of transitions to and from Si donor and acceptor states as well as other states in order to determine the relative number of donor and acceptor states before and after hydrogenation. Before hydrogenation we observed transitions between the donor states and triangular-well bound valence-band states near the surface. The acceptor-state transitions were to the unquantized conduction band. The many different signals present in our EER data were identified with the aid of bias studies -- studies of the dependence of the energy, strength, linewidth and lineshape of each signal on applied bias. Our new theory of high-field EER was used in this study as well as in our studies of ZnSe/GaAs and ZnSe/AlAs heterojunctions because the built-in field was too large before hydrogenation for the usual low-field theory to be valid.

Our EER study was complementary to the IPE study conducted by C. Coluzza et al. On the one hand, EER is not sensitive to very localized levels in the gap, but is sensitive to all shallow levels and resonances because of the relatively strong dependence of their energy on electric field. On the other hand, IPE measurements are sensitive to all optical transitions above the metal-to-semiconductor internal threshold to and from states at or near the interface (the original semiconductor surface), but not to transitions involving states away from the interface. This is because most photoexcited carriers created away from the interface recombine before reaching the Pd overlayer and thus do not contribute to the photocurrent.

In addition to the three topical investigations discussed above, which used primarily EER, we also performed several technique oriented projects not involving EER. We improved our SE experimental setup, developed new models and techniques for analyzing in-situ and ex-situ SE data, greatly improved our VER experimental setup, and performed an experimental and theoretical analysis of the basic physics of PR and VER so as to enhance their usefulness as optical nondestructive characterization techniques. The improvement of our phase modulated SE experimental setup primarily involved extending the spectral range down to 1.5 eV and up to 6.0

eV to match the range obtained using a rotating analyzer. A new, more accurate method for obtaining critical-point energies, linewidths and line shapes from SE data first proposed under DARPA contract #DAA03-86-K-0131 was extended. Also, a new model for the optical dielectric function of semiconductors was developed in order to (1) remove errors in the analytic form of previous models, (2) obtain accurate fits to SE data, and (3) interpolate between sets of SE data obtained at different compositions and/or temperatures to obtain accurate formulas for $\epsilon(\omega)$ as a function of composition and/or temperature. This work was largely motivated by the desire in the Microphysics Lab to use in-situ SE for diagnostic and control purposes during ME growth. This development of an accurate analytically correct model for the optical dielectric function should prove to be important both in connection with in-situ SE and in the design of optical and optoelectronic devices.

The VER technique was developed and a prototype experimental setup was constructed under DARPA contract #N00014-86-K-00070. Under the contract reported on here, that prototype setup was improved to obtain more precise positioning of the sample being studied, to allow measurements to be performed at low and high temperatures as well as at room temperature, and to remove interference fringes in the data caused by multiple reflections present in the prototype setup.

The idea for the instrument is simple: to use the original ER configuration of a parallel-plate capacitor, but using vacuum as the dielectric. The sample serves as one plate, and a semitransparent nickel electrode sputtered on a fused silica window forms the other plate, with vacuum in between. To obtain electric fields of 10^3 - 10^5 V/cm in the sample, fields one order of magnitude greater are required in the gap. Thus, the vacuum gap between the sample and the window must be small. Gaps of order 100 μm and voltages of several kV are used. For a well-defined, uniform electric field, the electrodes must be parallel. This makes the positioning and alignment of the sample critical. Given the magnitude of the electric fields needed, the vacuum must be good enough to prevent breakdown.

The development of this technique was motivated (1) by a desire to combine the advantages of EER and PR, while minimizing the disadvantages, (2) to measure under vacuum the differences between PR spectra and true ER spectra, and (3) to evaluate the effect, if any, of the dielectric fluid used in EER on the surfaces of samples. In particular the intention of this work was to develop a

purely ER form of measurement which would allow one to study spectra as a function of precisely known bias and applied modulating field or voltage, could be performed in vacuum from extremely low temperatures up to growth temperatures, and ultimately could be used in-situ.

The results of our VER measurements and some of our PR measurements were very surprising. In particular, we were not able to establish a significant dc bias in VER. Also, VER was more difficult experimentally than EER, and the data obtained from our original prototype setup was more difficult to analyze because of the presence of interference fringes throughout the spectral range. Thus, we limited our use of VER under this contract to (1) observing the differences between EER, VER and PR spectra obtained on the same samples under identical conditions, (2) studying the fundamental physical processes involved in VER and PR, (3) measuring the time constants involved in surface-state trapping and depletion-region transport processes, and (4) verifying the experimental results obtained by EER, especially for GaAs/Ga_{1-x}In_xP MQW's and superlattices. VER or PR studies of UN⁺ structures, in which the depletion region is characterized by a large, but constant, built-in electric field, allow one to measure the built-in field precisely. The results of our measurements on such samples suggested simple models for the fundamental physics of VER and PR. The application of nonequilibrium statistical mechanics along with transport theory in the lifetime approximation then led to mathematical predictions for the exact dependence of the VER and PR data on the VER and PR modulation amplitudes and frequencies, the applied dc bias (in the form of a constant external electric field), an applied dc laser intensity (another form of applied bias), the depletion depth and the magnitude of the built-in field. Further measurements were performed to test these predictions, and they were confirmed in every case.

The next section of this report contains a list of the publications and theses the research for which was supported in part or in whole by this contract. Following that is a list of our other publications which are of particular relevance to the work supported by this contract. Copies of the publications supported under this contract are enclosed. Copies of the theses supported under this contract are available upon request.

**PAPERS AND THESES SUPPORTED IN PART OR IN WHOLE
BY DARPA CONTRACT #n0014-89-j-3165**

- *1. L. Kassel, J. W. Garland, M. A. Haase and H. Cheng, "Effects of Zn and Ga Interdiffusion on ZnSe/N⁺GaAs Interfaces", *Semiconductor Science and Technology*, Vol. 6, No. 9A, pp. A146-A151, September 1991.
- *2. L. Kassel, J. W. Garland, P. M. Raccach, M. C. Tamargo and H. H. Farrell, "Electroreflectance Determination of the Band Profile of a ZnSe/n⁺GaAs Heterojunction", *Semiconductor Science and Technology*, Vol. 6, No. 9A, pp. A152-A156, September, 1991.
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- †4. C. Kim, J. W. Garland, H. Abad and P. M. Raccach, "Modeling The Optical Dielectric Function of Semiconductors: Extensions of the Critical-Point Parabolic- and Approximation", *Physical Review*, Vol. 45, No. 20, pp. 11749-11767, May 1992.
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- ‡10. S. L. Mioc, P. M. Raccah and J. W. Garland, "Vacuum Electroreflectance: Overcoming the Difficulties of Electrolyte Electroreflectance and Photorefectance", in Photo-Induced Space-Charge Effects in Semiconductors: Electro-Optics, Photoconductivity and the Photorefractive Effect, D. D. Nolte, N. M. Haeglina and K. W. Goosen, Editors, Proceedings of the Materials Research Society, Vol. 261, pp. 46-50, 1992
11. C. Kim, J. W. Garland and P. M. Raccah, "Modeling the Optical Dielectric Function of the Alloy System $Al_xGa_{1-x}As$ ", *Physical Review*, Vol. 47, No. 4, pp. 1876-1888, January 1993.
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- †13. J. W. Garland, C. Kim, H. Abad and P. M. Raccah, "Determination of Accurate Critical-Point Energies, Linewidths and Lineshapes from Spectroscopic Ellipsometry Data", *Thin Solid Films*, Vol. 233, No. 4, pp. 148-153, January, 1993.
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15. S. L. Mioc, J. W. Garland and R. Bennett, "Vacuum Electroreflectance and Photorefectance Study of a GaAs Structure with a Large Constant Built-in Field", IEEE Lasers and Electro-Optics Society 1993 Conference Proceedings, paper PD2.6, 1994.
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- †17. Hisham Abad, Thesis for the Doctor of Philosophy in Physics, University of Illinois at Chicago, 1991.
- *18. Laurent Kassel, Thesis for the Doctor of Philosophy in Physics, University of Illinois at Chicago, 1991.

- ‡19. De Yang, Thesis for the Doctor of Philosophy in Physics, University of Illinois at Chicago, 1991.
- †‡20. Charles Kim, Thesis for the Doctor of Philosophy in Physics, University of Illinois at Chicago, 1991.
- *21. Qi Ji Liu , Thesis for the Doctor of Philosophy in Physics, University of Illinois at Chicago, 1992.
- ‡22. Sylvia Mioc, Thesis for the Doctor of Philosophy in Physics, University of Illinois at Chicago, 1994.

- * The work reported in this paper (or thesis) was begun under DARPA contract #N00014-87-K-0296.
- † The work reported in this paper (or thesis) was begun under DARPA contract #DAAL03-86-K-0131.
- ‡ The work reported in this paper (or thesis) was begun under DARPA contract #N00014-86-K-0070.

**RELATED PAPERS AND THESES
SUPPORTED BY OTHER CONTRACTS**

1. P. M. Raccah, J. W. Garland, Z. Zhang, U. Lee, D.Z. Xue, L. L. Abels, S. Ugur, and W. Wilinsky, "Comparative Study of Defects in Semiconductors by Electrolyte Electroreflectance and Spectroscopic Ellipsometry", *Physical Review Letters*, Vol. 53, No. 20, pp. 1958-1961, November 1984.
2. P. M. Raccah, U. Lee, S. Ugur, D. Z. Xue, L. L. Abels and J. W. Garland, "Study of Mercury Cadmium Telluride (MCT) Surfaces by Automatic Spectroscopic Ellipsometry (ASE) and by Electrolyte Electroreflectance EER)", *Journal of Vacuum Science and Technology*, Vol. A3, No. 1, pp. 138-142, January -February 1985.
3. J. W. Garland and P. M. Raccah, "Generalized Theory of Electroreflectance with Applications to Materials Characterization", *Proceedings of the SPIE*, Vol. 659, pp. 32-42, 1986.
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SUMMARY OF RESULTS

The first project completed under this contract was the determination of the band profiles of ZnSe/GaAs and ZnSe/AlAs heterojunctions. The band profile is a mapping of the band edges as a function of distance from a sample surface or interface. Along with sample quality, band profiles are the primary factors determining the electrical and optoelectronic properties of advanced devices. In many cases, the detailed knowledge of a band profile offers a microscopic explanation of those properties most important to the device designer and/or growth expert. In particular, the band profiles measure the band offsets and electric fields at all interfaces, the surface pinning level, the charge densities caused by the interdiffusion of two species of atoms having different valences, and the diffusion length of each species for such interdiffusion. They are of practical importance because electric fields present at interfaces are detrimental for polar heteroepitaxial growth and because the charge imbalances caused by the interdiffusion of differently charged species cause barriers to hole or electron transport. Optical data are required for the detailed determination of band profiles.

Under this contract we analyzed ER, SE and Raman data on the last two of three sets of samples, with each sample consisting of a ZnSe film grown by M E on a III-V substrate or buffer layer, either GaAs or AlAs. In the first set of samples, supplied by M. A. Haase of 3M, the ZnSe was 100 nm thick and was unintentionally doped or p-doped with Li, and the substrate or buffer layer was heavily p-doped. Three of these samples were studied. In the two samples in the second set, also supplied by M. A. Haase, the ZnSe epilayers were grown on heavily n-doped ($n = 1\text{--}4 \times 10^{18} \text{ cm}^{-3}$) GaAs. The ZnSe thicknesses were 140 nm and 90 nm for samples 1 and 2, respectively. The ZnSe was heavily n-doped ($n = 4 \times 10^{18} \text{ cm}^{-3}$) with Cl over the 45-50 nm closest to the substrate in sample 1 and was unintentionally doped in sample 2. The two samples in the third set, which was supplied by M.C. Tamargo of ellcore, each consisted of 100 nm of unintentionally doped ZnSe grown by M E on heavily n-doped ($n = 3\text{--}6 \times 10^{18} \text{ cm}^{-3}$) GaAs substrates.

The conduction band offset was found to be approximately 0.3 eV. We found the Ga diffusion length to be approximately 4 nm and the Zn diffusion length to be approximately 10--11 nm in all of the samples. For sample 2 of set 2 and both samples of set 3, the charge density of

interdiffused ionized Zn atoms was found to be approximately $1.0 \times 10^{13} \text{ cm}^{-2}$, and that for interdiffused Ga atoms was found to be approximately $4 \times 10^{12} \text{ cm}^{-2}$. For sample 1 of set 1 the corresponding charge densities were found to be $1.4\text{--}1.5 \times 10^{13} \text{ cm}^{-2}$ and $1.1\text{--}1.2 \times 10^{13} \text{ cm}^{-2}$. For sample 2 of set 2 and both samples of set 3 the interdiffusion produced a rounded barrier to electron flow on the GaAs side of the interface approximately 20 nm thick and reaching a maximum height of 0.2--0.3 eV above the Fermi level.

For all four samples, the electric fields were found to be almost the same on opposite sides of the heterointerface, implying that the interfacial charge densities were much smaller than the two dimensional charge densities produced by interdiffusion, approximately 10^{12} e/cm^2 . Those fields were found to be approximately $1 \times 10^6 \text{ V/cm}$ for sample 1 of set 1 and approximately $6 \times 10^5 \text{ V/cm}$ for the other three samples. The larger interdiffusion in sample 1 of set 2 was attributed to the Cl doping of the ZnSe in that sample; the diffusion length of the Cl in ZnSe was found to be approximately 3 nm, similar to but somewhat smaller than that of the Ga in ZnSe.

The Raman measurements of the maximum fields on either side of the ZnSe/GaAs heterointerfaces were in agreement with the values obtained from our EER measurements. Also, the Raman determinations of the relative quality of the different samples were in agreement with our EER measures of quality. Finally, the Raman studies revealed no signs of Zn_3As_2 , Ga_2Se_3 , Se or Ga islands, although similar Raman studies have revealed such islands in samples grown by other techniques.

The band profiles calculated from our data are consistent with the electrical data of other researchers as well as that of M. A. Haase, if one assumes the interdiffusion to increase with increasing growth temperature, as is expected. However, they are totally different from the simple model band profiles assumed by other researchers, differing even in the sign of the conduction-band offset. In agreement with theoretical calculations, we found the ZnSe/GaAs interface to be type 1, whereas other researchers were led by the overly simplified band profiles which they assumed to find the interface to be type 2.

The band profiles calculated from our data show that interdiffusion creates a significant barrier to current flow across the ZnSe/GaAs heterointerface and show that the strength of that barrier increases with Cl doping of the ZnSe. That barrier was found to be the primary cause of the high resistivity which has limited the usefulness of ZnSe/n⁺GaAs devices, in particular blue-light-

emitting diodes. M. A. Haase has stated that these results were very important in leading his group to be the first to produce a blue-green semiconductor laser.

This project is reported on in detail in papers 1 and 2 in the list of papers and theses supported by this project and in the thesis of L. Kassel, number 18 on the list; the Raman work on this project is reported in detail in the thesis of Qi Ji Liu, number 21 on the list. The method used for the construction of the band profiles also is reported in paper 8 on that list.

A major project performed under the sole support of this contract was the first measurement by ER of the band offset of lattice-matched GaAs/Ga_{0.51}In_{0.49}P MQW's and superlattices. The values $\Delta E_c = 159 \pm 4$ meV and $\Delta E_v = 388 \pm 6$ meV were obtained for the conduction and valence-band discontinuities, respectively.

The samples provided by M. Razeghi of Northwestern University were of exceptional quality, enabling us to observe an extraordinarily large number of transitions. For the three-quantum-well sample, which contained wells of three different thicknesses, we observed and measured the energies of 28 different transitions, three band-to-band transitions, 16 transitions in the 12 nm quantum well, 6 transitions in the 6 nm quantum well, and 3 transitions in the 3.5 nm quantum well. The superlattice consisted of ten periods of 9 nm thick GaAs wells between Ga_{0.51}In_{0.49}P barriers approximately 10 nm thick. Because of the width of the barriers, the well subbands were very narrow, of order 1 meV or less in width. Thus, we observed only the spectrum associated with a single quantum well, with the spectral lines widened by approximately 1 meV. We observed 38 different transitions, including 3 band-to-band transitions, 20 well-state to well-state transitions and 15 crossover transitions between well states and barrier band edges.

Of the twenty well-state to well-state transitions observed, ten were weak transitions forbidden by symmetry in the absence of an electric field. Those transitions were easily distinguished by the strong dependence of their amplitudes on the applied bias. The crossover transitions between well states and the tails of band states at the barrier edges were easily distinguished by the strong dependence on bias of their widths. Our final identification of each transition was accomplished by performing a parameterized first-principles calculation of all the well-state energies using a program supplied by W. Poetz of our lab, treating all of the relevant masses as parameters. The values found for the conduction-band, heavy-hole and light-hole masses and the split-off mass in both the GaAs wells and the Ga_{0.51}In_{0.49}P were in excellent agreement with

the other values found in the literature. The conduction-band and valence-band discontinuities were obtained directly from the observed transition energies, using only the theoretical value of the first heavy-hole well state, which is known very accurately. The intraband, intersubband transition energies, which are needed for the design of III-V infrared detection devices were determined simply by subtracting two observed interband transitions from one another. These were the first recorded direct measurements of the intersubband, intraband transition energies or of the band discontinuities for type I superlattices or quantum wells.

This project is reported on in detail in paper 6 in the list of papers and theses supported by this project and in the thesis of D. Yang, number 19 on the list.

The other materials and device oriented investigation which we performed under the sole support of this contract was a study of the effect of surface bombardment with H_2 molecules on n-type Si-doped GaAs. This investigation was carried out in collaboration with C. Coluzza, who supplied the samples and performed internal photoemission (IPE) measurements on the same samples after growing Pd Schottky barrier structures on them.

Our EER study revealed the presence of shallow levels in the gap. A bias study helped to distinguish between acceptor and donor levels. Before hydrogenation both acceptor and donor states, probably both Si dopant states, were observed, with the number of donor states being larger. Hydrogenation totally passivated the acceptor level and largely passivated the donor level, but induced a new level with binding energy intermediate between those of the donor and acceptor levels. Our EER results also clearly indicated that hydrogenation induces a resonant state either in the valence band or in the conduction band. Presumably these two new levels arise from the passivated donor and acceptor levels. They were also observed in the 77 K IPE spectra, although in the IPE spectra the resonant level seen by EER was shifted from just above E_0 to just below E_0 . Because the interest in this study was in localized levels, there was no need to use the high-field theory; transitions to and from such levels give EER spectra properly described by the low-field theory, with the dominant term in the lineshape being the first-derivative term.

This investigation is reported on in detail in paper 3 in the list of papers and theses supported by this project, and in the thesis of L. Kassel, number 18 on the list.

The SE work performed under this contract primarily fell into the following three categories: (1) the development, testing and use of a new technique for the analysis of SE data, (2)

the improvement of our experimental SE setup and the testing of the accuracy of data obtained from that setup, and (3) the development of a new, greatly improved model for the optical dielectric function of semiconductors. Most of the work in category (1) was performed under DARPA contract #DAAL03-86-K-0121, but under this contract that work was extended and reported on at the First International Conference on Spectroscopic Ellipsometry, at which it generated more interest than almost any other paper. This work was summarized in the final report on DARPA contract #DAAL03-86-K-0131 and is reported in detail in papers 4 and 13 in the list of papers and theses supported by this project and in the theses of H. Abad and C. Kim, numbers 17 and 20 on the list.

The improvement of our experimental SE setup was performed under the sole support of this contract. It enabled us to extend the spectral range of our SE spectra down to 1.4 eV and up to 6.0 eV. That allowed us to perform SE measurements around E_0 in GaAs and around E_1 in such wide-gap semiconductors in ZnSe. That improvement and the accuracy of the data obtained are reported in detail in paper 5 in the list of papers and theses supported by this contract, and in the thesis of C. Kim, number 20 on the list.

The development of a new model for the optical dielectric function of semiconductors, $\epsilon(\omega)$, also was performed under the sole support of this contract. This work was entirely theoretical in character. The new model is more generally valid than any of the previous models -- the harmonic-oscillator model, the critical-point model or the model of Adachi. It is applicable over the entire range of photon energies, below and above the band gap, correctly incorporates the electronic band structure of the medium, and exactly satisfies the Kramer-Kronig transformation. Among other improvements, it corrects a long-standing error in the literature in the general formula used for $\epsilon(\omega)$, replacing a factor ω^{-2} by the correct factor $[E_c(\mathbf{k}) - E_v(\mathbf{k})]^{-2}$, where $E_c(\mathbf{k})$ and $E_v(\mathbf{k})$ are conduction- and valence-band energies for the wavevector \mathbf{k} . As a result, it yields an imaginary part of $\epsilon(\omega)$ which correctly goes to zero as ω approaches zero, rather than going to infinity. The model goes beyond the parabolic-band approximation in that it correctly takes into account the full analytic form of the electronic density of states and thus does not require the use of arbitrary cutoff energies. The primary parameters of the model, unlike those of the harmonic oscillator model, are physically significant, and all of its parameters vary smoothly and are easily found from SE data as simple analytic functions (low-order polynomials) of composition and temperature. Also, it is

unique in allowing one to simultaneously fit $\epsilon(\omega)$ and its derivatives with respect to ω , and in allowing one to go beyond the usual approximation of Lorentzian broadening which is known to be incorrect for elements and compounds above very low temperatures. It yields much better fits to experimental results for $\epsilon(\omega)$ and its derivatives than does any previous model.

Under this contract the new model was applied to GaAs and to the alloy systems $\text{Al}_x\text{Ga}_{1-x}\text{As}$. After the conclusion of this contract, it has been improved further and has been applied to other semiconductors, including CdTe and ZnSe. It was found to yield extremely accurately the optical properties of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ over the entire photon range from 1.5 eV to 6.0 eV and over the entire composition range from $x = 0$ to $x = 1$. It also allows one to calculate the refractive indices rather accurately over the entire composition range below 1.5 eV, without the use of any optical data below 1.5 eV.

The comparison of our model with SE data strongly supports the theoretical conclusion that the line-shape broadening in GaAs at room temperature is more nearly Gaussian than Lorentzian. That comparison also strongly suggests that far above E_0 , where the probing light does not penetrate far below the surface of a sample, the surface boundary condition on electronic wave functions prevents SE from measuring the true bulk dielectric function. It supports the theoretical conclusion that this boundary condition results in an experimentally measured $\epsilon(\omega)$ in which the true $\epsilon(\omega)$ is multiplied by a phase factor, admixing its real and imaginary parts.

The new model for the optical dielectric function and its applications performed under this contract are reported in detail in papers 4 and 11 in the list of papers and theses supported under this contract, and in the thesis of C. Kim, number 20 under this contract.

The final project performed under this project was an improvement of the prototype apparatus for VER, originally constructed under DARPA contract #N00014-86-K-0070. In the new VER apparatus, the sample is interferometrically aligned and precise positioning is achieved with piezoelectric motors. Cooling to 80K is accomplished using the Joule-Thompson effect, and temperatures up to 400 K are achieved using resistive heating. As in the original apparatus, the sample surface serves as one plate of a dielectric and a semitransparent electrode sputtered on a fused silica window forms the other, with vacuum in between. A modulating electric field and a dc bias field are applied to the surface of the sample by applying suitable voltages to the semitransparent electrode. Gaps of order $100\mu\text{m}$ and voltages of several kV are used.

Data were first taken on semi-insulating, lightly doped and heavily doped GaAs in order to compare the VER, EER and PR spectra. EER spectra could not be obtained for the semi-insulating sample, because the applied modulating voltage was dropped across the entire sample, leading to a very small modulating field. For that sample the VER and PR line shapes were very similar somewhat above and in the immediate vicinity of E_0 , but the VER spectra showed a strong peak about 40 meV below E_0 , which was absent in the PR data, although it had been seen in PR data by other researchers on other semi-insulating GaAs samples. This peak changed sign upon going from room temperature to 80K or upon decreasing the modulation frequency from 2 kHz to 151 Hz, and was very sensitive to polishing damage on the back of the sample.

To obtain a comparison with EER, the measurements were repeated on a lightly doped (mid 10^{16} cm^{-3}) sample, both around E_0 and around E_1 . Around E_0 , the EER, VER and PR spectra looked similar, except for the peak 40 meV below E_0 . Around E_1 , the EER and VER spectra were essentially identical, and both could be accurately fit by the low-field ER theory. However, the PR spectra was substantially different, and could not be fit by the ER theory. For higher doping levels ($N_d = 1.2 \times 10^{17} \text{ cm}^{-3}$ and $N_d = 1.2 \times 10^{18} \text{ cm}^{-3}$), all three spectra were qualitatively similar. For the lesser doped sample, the EER and VER spectra were essentially the same, but for the more heavily doped sample, which has a depletion region only about 30 nm thick, the two E_0 spectra were markedly different. We interpreted that difference as arising from the difference between the vacuum and electrolyte surface boundary conditions, which would significantly affect the spectra for this sample, in which the quantized valence-band depletion-well levels are widely separated for small n . For both samples, the PR spectra were similar to the VER spectra, but with a much stronger first-derivative component arising from the modulation of the critical-point energies by the photoexcited electron-hole pairs which modulate the built-in field.

Later, under university support, UN^+ Ga As samples were obtained from R. Ennett at the Naval research Lab. In those samples the built-in electric field in the depletion region is constant, so that it can be precisely measured by ER or PR. Many VER and PR measurements, and a few EER measurements, were performed on those samples. The VER measurements were performed in both air and vacuum as a function of modulation amplitude and frequency and as a function of the strength of a superimposed dc laser illumination. The PR measurements were performed as a function of the amplitude and frequency of the modulating laser illumination. The

magnitude of the measured spectra and the values of the IF were studied as functions of the experimental variables.

The IF measured by VER at low modulation fields was found to be higher in vacuum, but that measured by PR was found to be lower in vacuum. Variation of the modulation frequency f , produced similar, although quantitatively different, strong effects in VER and PR, but not in EER. Below a certain threshold frequency, the signal amplitude was greatly reduced with decreasing f , by two orders of magnitude as f approaches zero. We interpreted this effect as arising from dynamic screening of the modulation of the IF, approaching near-total screening as f approaches zero and thus eliminating virtually all effects of any dc bias. The screening arises through the tunneling of conduction-band electrons to surface-state holes and hence is only effective at low f . Related effects on the IF were also observed.

The IF also was found to decrease very rapidly with increasing laser illumination, up to approximately that illumination required to obtain a good PR signal, and then to continue to decrease with further increasing illumination, but an order of magnitude more slowly. This effect was observed for both VER and PR, although it was quantitatively different for the two cases. It was attributed to a screening of the IP by photo-excited electron-hole pairs, with the holes drifting to the surface and being trapped there. The laser illumination was also found to enhance the tunneling of electrons to surface-state holes and thus the dynamic screening of the modulation, raising the frequencies at which it becomes effective.

These VER investigations are reported in detail in papers 7, 10, 14, 15 and 16 in the list of papers and theses supported under this contract, and in the thesis of S. L. Mioc, number 22 on the list. Recently a detailed mathematical model of VER and PR has been constructed by the principal investigator. This model has explained quantitatively all of the effects mentioned above, including all of the differences observed between VER and PR. It also has predicted other effects and dependences not seen previously, which have now been verified experimentally. That work will be submitted for publication shortly.

REPORT OF INVENTIONS AND SU CONTRACTS

No inventions were made or patent applications filed related in any way to the work performed under this contract. No subcontracts were awarded under this contract.

THE VIEWS, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHORS(S) AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE NAVY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.