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ZnSe was doped with Ga to electron concentrations in the low 10<sup>17</sup> cm<sup>-3</sup> range. It was determined that optimum doping occurred for a Se:Zn flux ratio of close to unity as measured with a quartz crystal monitor. DLTS measurements indicated that delta doped samples had an order of magnitude less deep level traps than uniformly doped samples. Monte Carlo simulations of the growth kinetics of ZnSe, combined with absolute flux measurements, provided information about sticking coefficients and insight into stoichiometric growth conditions. The nucleation of epitaxial ZnSe on epitaxial GaAs was studied for the first time. MISFET devices were fabricated, and MIS capacitor C-V characteristics were used to evaluate the properties of the heterovalent interface. Techniques were found by which interface state densities were reduced to values comparable to (Al,Ga)As. Monte Carlo Method; MISFET Semiconductors; Lattice Dynamics. (CP)

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**AIR FORCE OFFICE OF SCIENTIFIC RESEARCH**

**FINAL REPORT**

**for period July 1, 1985 to June 30, 1989**

**GRANT NO. 85-0185**

**entitled**

**"II-VI SEMICONDUCTOR SUPERLATTICES"**

**by**

**Professor Robert L. Gunshor, Co-Principal Investigator  
School of Electrical Engineering**

**and**

**Professor Nobuo Otsuka, Co-Principal Investigator  
Materials Engineering  
Purdue University  
West Lafayette, IN 47907**

## SUMMARY OF TECHNICAL ACTIVITIES

There has been a continued close overlap between the MBE and TEM activity over the period of the report; the degree of overlap in the two activities is evident in the publication list. In addition, the TEM has acted as a center for TEM studies of semiconductor interface formation for a number of other MBE groups including those of H. Morkoc and J. Schetzina.

A considerable activity during the first part of the reporting period involved the installation of new equipment. The MBE facility acquired a three growth chamber modular MBE, and the TEM group saw the installation of a new high resolution TEM. The normal research activity continued through this period, and included work on Monte Carlo simulations of growth kinetics for ZnSe as well as the beginning of an effort to incorporate Ga into ZnSe as an n-type dopant. (Publications are listed in the appropriate section of the report.) The doping activity included attempts at photoassisted doping. In our experiments, the effects of laser illumination were overshadowed by the dramatic improvements associated with optimization of the incident flux ratio. Our experiments tended to suggest that the main role of illumination in the case of CdTe photoassisted doping was that of optimizing the surface stoichiometry; an observation which was recently confirmed by reports at the 1989 International II-VI conference.

The TEM group developed a useful iodine thinning technique in collaboration with an apparatus equipment manufacturer (Gatan, Inc.). The use of an iodine thinning stage following Ar milling has proved to be vital for work with the easily damaged II-VI compounds. The present level of development of sample preparation has resulted in II-VI TEM images having quality comparable to those obtained from III-V samples. The second year also saw completion of the Monte Carlo simulation effort, which, when combined with an absolute measure of incident flux ratio during growth, was able to focus on such issues as sticking coefficient. The results enabled us to find the growth conditions for obtaining highly stoichiometric ZnSe epilayers. Predictions also included significant variations in epilayer structure depending upon the molecular form of the Se flux. The predictions were confirmed by the recent experiments of MBE groups employing Se cracking.

The work on the Ga doping of ZnSe was essentially completed during the third year. A considerable amount of transport and photoluminescence data was obtained. The effort was then extended beyond uniform incorporation to include the delta doping of Ga in ZnSe. The delta doping technique had been shown by the Bell Core group to result in higher carrier concentration levels for a given amount of Ga. We (in collaboration with R.F. Pierret) extended their work to include DLTS measurements. These experiments demonstrated that the delta doping technique resulted in a ten-fold reduction in deep level trap densities. The DLTS work is described in an attached reprint.

The focus of the fourth year was on the details of formation of the ZnSe/GaAs interface. This period also saw the acquisition of a high resolution XPS system as a component of the

modular MBE. The motivation for this addition was our interest in the details of the bonding occurring at II-VI/III-V heterovalent interfaces. The importance of this interface was amplified by our discovery of an ex situ annealing procedure which resulted in ZnSe/GaAs MIS capacitors having integrated interface state densities as low as values reported for (Al,Ga)As structures. Just prior to the end of this reporting period we discovered a growth technique for the formation of ZnSe/GaAs interfaces having low interface state densities in as-grown structures. The significance of this result was that we could achieve low interface state densities without the necessity of a post-growth annealing procedure. At the same time, the TEM studies provided the first clues that the formation of Ga<sub>2</sub>Se<sub>3</sub> interfacial layers were associated with interfaces exhibiting optimized electrical properties.



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**PUBLICATIONS LIST**  
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**Serial Journal Articles (contributed and invited)**

- [1] L.A. Kolodziejski, R.L. Gunshor, S. Datta, T.C. Bonsett, M. Yamanishi, R. Frohne, T. Sakamoto, R.B. Bylisma, W.M. Becker, and N. Otsuka, "MBE Growth of Films and Superlattices of Diluted Magnetic Semiconductors," *J. Vac. Sci. and Tech.*, B3 pp. 714-717 (1985).
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- \*[51] R.L. Gunshor, A.V. Nurmikko, L.A. Kolodziejski, M. Kobayashi, and N. Otsuka, "Wide-Gap II-VI Heterostructures" to appear in *Journal of Crystal Growth*.

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### Conference Presentations (contributed and invited)

- [1] D. U. Bartholomew, E. K. Suh, L. A. Kolodziejski, R. L. Gunshor, and A. K. Ramdas, "Raman Scattering from Diluted Magnetic Semiconductor Superlattices," presented at the *APS March Meeting*, Las Vegas (1986).
- [2] L. A. Kolodziejski, R. L. Gunshor, N. Otsuka, S. Datta, "MBE of II-VI Semiconductors," presented (L.A.K.) at *Materials Research Society Spring Meeting*, Palo Alto, (1986). [INVITED]
- [3] L. A. Kolodziejski, Y. Hefetz, D. Lee, R. L. Gunshor, and A.V. Nurmikko, "Ultrathin Compositional Modulation Within ZnSe/(Zn,Mn)Se Superlattices," *Amer. Phys. Soc. March Meeting*, Las Vegas, (1986).
- [4] Y. Hefetz, W. C. Goltsos, A. V. Nurmikko, L. A. Kolodziejski, and R. L. Gunshor, "Exciton formation and energy exchange with d-electron states in ZnSe/(Zn,Mn)Se multiple quantum wells," presented at *APS March Meeting*, Las Vegas, (1986).
- [5] A. V. Nurmikko, Y. Hefetz, R. L. Gunshor, and L. A. Kolodziejski, "Optical Properties of Magnetic Semiconductor Quantum Wells," presented at the *International Conference on Quantum Electronics*, San Francisco, June (1986). [INVITED]
- [6] L. A. Kolodziejski, R. L. Gunshor, A. V. Nurmikko, and N. Otsuka, "RHEED Oscillations and the Epitaxial Growth of Quasi - 2D Magnetic Semiconductors," presented at the NATO Advanced Research Workshop on "Thin Film Growth Techniques of Low Dimensional Structures," Brighton (England), September (1986). [INVITED]
- [7] S.-K. Chang, A. V. Nurmikko, L. A. Kolodziejski, and R. L. Gunshor, "Differences in Optical Properties of (111) and (100) Oriented CdTe/(Cd,Mn)Te Multiple Quantum Wells," *Bull. Am. Phys. Soc.*, 31, pp. 653 (1986), - presented at the *APS Meeting*, Las Vegas, March (1986).
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- [9] Y. Hefetz, W. C. Goltsos, D. Lee, A. V. Nurmikko, L. A. Kolodziejski, and R. L. Gunshor, "Electronic Energy States and Relaxation in  $Zn_{1-x}Mn_xSe$  Superlattices," - presented at the *2nd Int'l. Conf. on Superlattices, Microstructures and Microdevices*, Goteborg, Sweden, Aug. 17-20, 1986.
- \*[10] R. L. Gunshor, L. A. Kolodziejski, N. Otsuka, S. Datta, and A. V. Nurmikko, "Submicron Heterostructures of Diluted Magnetic Semiconductors," presented at the *Materials Research Society Symposium*, Boston, December (1986). [INVITED]
- [11] R. L. Gunshor, L. A. Kolodziejski, N. Otsuka, B. P. Gu, D. Lee, Y. Hefetz, and A. V. Nurmikko, "2D Metastable Magnetic Semiconductor Superlattices," - presented at the *2nd Int'l. Conf. on Superlattices, Microstructures*

- and Microdevices, Goteborg, Sweden, Aug. 17-20, 1986.*
- [12] L. A. Kolodziejski, R. L. Gunshor, N. Otsuka, B. P. Gu, Y. Hefetz, and A. V. Nurmikko, "Use of RHEED Oscillations for the Growth of 2D Magnetic Semiconductor Superlattices (MnSe/ZnSe)," - presented at the *IV Int'l. Conf. on Molecular Beam Epitaxy*, York, England, Sept. 7-10, 1986.
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