

Wide bandgap II-VI materials have important technological potential, for example, as short wavelength (visible to ultraviolet) optical sources with applications in optical recording and bright emissive displays. A recent key advance in the area of Zn chalcogenides involves successful p-type doping of ZnSe-based semiconductors using nitrogen as acceptor species (first reported by Park et al.¹). This led to the achievement of a pn diode injection laser operating at blue/blue-green wavelengths by Haase et al.² and Jeon et al.³ These structures consisted of (Zn,Cd)Se narrow bandgap well layers with Zn(Se,S) cladding barrier layers, although more recent structures are composed of barrier layers of (Zn,Mg)(Se,S).⁴ To minimize defect generation within the active regions of the device, as well as to maximize the incorporation of the nitrogen acceptor species, the substrate temperatures have been reported to be extremely low (~150-250°C). By employing gas source epitaxy technologies for the growth of the aforementioned quantum well structures, control of the constituent species via precision mass flow controllers is anticipated to offer a solution to the difficulties encountered in the MBE of materials containing one or more high vapor pressure species. In addition, as the growth temperature is lowered, control of the flux ratio will become even more crucial.

The use of a beam-assisted growth approach in conjunction with metalorganic molecular beam epitaxy provides us with the capability of lateral patterning as well as composition modulation in the growth direction, which cannot be achieved by conventional MBE. To address some of these materials-related issues, we have embarked on a II-VI-based research program which emphasizes growth by the gas source epitaxy approach of various heterostructures which can be used for visible light emitters.

In section 4.2 we describe the progress that we have made in understanding the photo-assisted MOMBE growth of ZnSe using a combination of solid and gaseous MO sources with various energies of impinging photons. The laser-assisted growth technique was instrumental in aiding our understanding of the complex surface chemistry

which was occurring that limits the growth when using particular MO sources. The II-VI effort is complemented by a new research program with a research goal of fabricating lattice-matched epitaxial buffer layers of (In,Ga)P (section 4.3). The recently functioning III-V GSMBE is also being utilized to begin the investigation of very sophisticated (In,Ga)(As,P) waveguide devices for application as tunable filters operating at 1.55 μm which is the wavelength of interest for optical fiber communication (section 4.4).

3.2 Photo-Assisted Metalorganic Molecular Beam Epitaxy of ZnSe Using a Combination of Solid and Gaseous Sources

Sponsors

3M Company Faculty Development Grant
 Defense Advanced Research Projects Agency
 Subcontracts 216-25013 and 542383
 Joint Services Electronics Program
 Contract DAAL03-92-C-0001
 National Science Foundation
 Grant ECS 88-46919
 Grant ECS 89-05909

The use of photon illumination during the epitaxial growth of compound semiconductors enhances the capabilities of conventional growth techniques by modifying the surface chemistry and thus providing a potential tool necessary for in-situ selective area epitaxy. Photo-assisted epitaxy has been reported for the growth of both narrow and wide bandgap II-VI materials, as well as for a variety of III-V semiconductors. The effect of photons on the growth is dependent on the precursor selected for constituent materials (and/or the type of growth technology employed), as well as the energy and flux of illuminating photons.

The various physical mechanisms which have been either reported or verified experimentally to explain the effect of photon illumination include: (1) selective desorption of adsorbed surface species, (2) pyrolysis of source precursors at the surface via

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- 1 R.M. Park, M.B. Troffer, C.M. Rouleau, J.M. Depuydt, and M.A. Hasse, "P-Type ZnSe by Nitrogen Atom Beam Doping during Molecular Beam Epitaxial Growth," *Appl. Phys. Lett.* 57: 2127-2129 (1990).
 - 2 M.A. Hasse, J. Qui, J.M. Depuydt, and H. Cheng, "Blue-Green Laser Diodes," *Appl. Phys. Lett.* 59: 1272-1274 (1991).
 - 3 H. Jeon, J. Ding, W. Patterson, A.V. Nurmikko, W. Xie, D.C. Grillo, M. Kobayashi, and R.L. Gunshor, "Blue-green Injection Laser Diodes in (Zn,Cd)Se/ZnSe Quantum Wells," *Appl. Phys. Lett.* 59: 3619-3621 (1991).
 - 4 H. Okuyama, T. Miyajima, Y. Morinaga, F. Hiei, M. Ozawa, and K. Akimoto, "ZnSe/ZnMgSSe Blue Laser Diode," *Electron. Lett.* 28: 1798-1799 (1992).

increases in the substrate temperature, (3) direct photolysis of source precursors which are present in the gas phase, and (4) photo-catalysis of molecular species through the creation of free carriers present at the surface. Similar effects on the epitaxial growth process have been reported when the surface is illuminated with an electron beam. In the case of an electron beam, the physical mechanisms which have been postulated include kinetically-induced decomposition of adsorbed precursor molecules and/or the presence of charge carriers which interact with surface species.

In this program, the effect of "beam-assisted" growth during the metalorganic molecular beam epitaxy (MOMBE) of ZnSe is under investigation. By utilizing the wavelength-dependent laser-assisted growth technique and a combination of both gaseous metalorganic and solid elemental sources during the growth, we were able to identify the dominant surface reactions which result in significant enhancements in the growth rate, as well as a growth rate suppression.

ZnSe films were grown by MOMBE on GaAs(001) substrates. The Zn and Se precursors included elemental (6N) Zn and Se, diethylzinc (DEZn), dimethylzinc (DMZn), and diethylselenium (DESe). DEZn and DESe were initially chosen due to their lower thermal decomposition energies to enable the low temperature growth of ZnSe. The DEZn was typically utilized as a metalorganic gas, i.e. not thermally decomposed, with quadrupole mass spectroscopy of the gas beam indicating that thermal decomposition occurs near 300°C. In all cases, the DESe molecule was thermally decomposed at 800°C prior to impingement onto the substrate surface. The calibrated substrate temperature ranged from 150-475°C. Photo-assisted MOMBE was performed by illuminating a portion of the wafer's surface with laser radiation. The emission lines of an argon ion laser, a Ti:sapphire laser (7800 Å), and a dye (Coumarin 7) laser were all used to investigate the wavelength dependence of the photo-assisted growth. The power density of the lasers was kept very low (<200 mW/cm²), eliminating the possibility of photon-induced thermal pyrolysis of the metalorganic precursors.

The unilluminated growth rate using DEZn and DESe precursors was found to be abnormally low (several hundred angstroms per hour) for variations in the following growth parameters: substrate temperature, gas flow rate, the VI/II flow rate ratio, the

addition of hydrogen supplied by a gas injector, and the thermal pyrolysis of each gaseous species using a "cracking" gas injector. The growth parameter-independent low growth rate suggested that the growth rate was limited not by mass transport to the substrate surface, but rather that the Zn and Se atoms were unable to incorporate into the crystalline lattice. However, we found that illumination with photons having energy greater than the energy bandgap of the ZnSe, was found to significantly increase the growth rate under certain conditions. To verify that the resultant low growth rate and high illuminated growth rate was unique to the use of diethyl-based metalorganic sources, ZnSe was grown with all combinations of DEZn, DMZn, DESe, and elemental Zn and Se. Growth rates obtained using atomic Zn or DMZn and elemental Se were typical of that achievable with molecular beam epitaxy and limited only by mass transport to the substrate surface; however, when at least one diethyl metalorganic was used, the resultant unilluminated growth rate was very low. The experimental evidence thus suggested that the presence of ethyl radicals (or a byproduct of diethyl molecular decomposition) was responsible for the low unilluminated growth rate. The ethyl radicals are believed to be strongly chemisorbed to the ZnSe surface such that the incorporation sites for the metal atoms were not available. Relatively high substrate temperatures were investigated (up to 475°C) in an attempt to desorb the ethyl species responsible for surface site saturation. The measured growth rate was extremely low, ~100 Å/hour. We speculate that the desorption rate of the ethyl species was not significantly modified at the high substrate temperatures, whereas the desorption of Zn and Se became significant and dominated the growth. Work reported in the literature describing the chemical beam epitaxy of GaAs by Murrell et al.⁵ has indicated that a similar surface site blockage phenomenon was speculated to occur at relatively low substrate temperatures for GaAs.

The generation of free carriers at the growth front during MOMBE growth has been found to alleviate the site blockage phenomenon encountered using DEZn and DESe sources. In addition, new degrees of freedom are provided for the selection of the growth conditions. Depending on the degree of pyrolysis of the Zn source, the application of a laser was found to induce either an enhancement or a suppression of the growth rate. The influence of the laser on the growth rate for the various combinations of sources employed is summarized in table

⁵ A.J. Murrell, A.T.S. Wee, D.H. Fairbrother, N.K. Singh, J.S. Foord, G.J. Davies, and D.A. Andrews, "Surface Chemical Processes in Metal Organic Molecular-Beam Epitaxy: Ga Deposition from Triethylgallium on GaAs (100)," *J. Appl. Phys.* 68: 4053-4063 (1990).

Source of Zn	Source of Se	MOMBE Growth Rate*	Effect of Illumination on Growth Rate
DEZn	DESe	No Growth	None
DEZn	cracked DESe	Low	Enhancement
DEZn	elemental Se	Low	Enhancement
elemental Zn	cracked DESe	Low	Suppression
cracked DEZn	cracked DESe	Low	Suppression
elemental Zn	elemental Se	High (MBE)	Suppression
cracked DMZn	cracked DESe	Low	Enhancement
cracked DMZn	elemental Se	High	Suppression or Enhancement

* Low: 100 - 400 Å/hr. High: typical of MBE

Table 1. Comparison of the growth rate of ZnSe obtained for various source materials and with application of photons having energy sufficient to generate carriers.

1. An enhanced growth rate was observed for growth conditions which resulted in partially pyrolyzed DEZn at the surface. Thermal decomposition of the DEZn prior to delivery to the substrate surface resulted in the expected low unilluminated growth rate (as shown in table 1). However, in stark contrast to the results described for the unpyrolyzed DEZn molecule, a suppression of the illuminated growth rate was observed. From these qualitative observations, it is clear that the surface chemistry which dominated the laser-assisted MOMBE growth was the conversion of partially pyrolyzed DEZn into atomic Zn which leads to incorporation into the lattice. When using DMZn and solid Se, we have measured both growth rate enhancement and suppression depending on the growth conditions which result in various surface stoichiometries. A laser-assisted effect was also observed when a more "MBE-like" growth approach was used, i.e., both metalorganic sources were cracked and/or solid sources were employed. In these cases, however, the illuminated growth rate was measurably suppressed and was in agreement with earlier reports of laser-assisted MBE growth of ZnSe.⁶ We attributed the growth rate reduction to the desorption of excess Se on the surface. Variations of the energy of the impinging photons in the "MBE-like" growth approach also confirmed that the desorption phenomenon was related to the genera-

tion of electron/hole pairs and the presence of free carriers at the growth front.

Low temperature photoluminescence (PL) was used to assess the optical properties of the thin ZnSe films. Ultraviolet radiation from a He-Cd laser was used as the excitation source while keeping the sample temperature near 10K. Figure 2 shows the PL obtained from the illuminated (photons having $\lambda = 4579 \text{ \AA}$) and unilluminated regions of the film when cracked DESe and uncracked DEZn were used as the source materials. The PL data demonstrates the effect that the laser has on the growth. The thin ZnSe film, which was not illuminated by the laser (upper curve), is dominated by deep level defects suggesting a highly nonstoichiometric layer. In contrast, the film grown with photon illumination (lower curve) shows practically no deep level luminescence and a remarkably more intense near bandedge feature, most likely a bound exciton with an energy of 2.796 eV. Identification of the impurity related to the formation of the exciton is complicated by the presence of strain and requires additional investigation. Figure 3 shows the PL for a film grown with solid Zn and cracked DESe, at a calibrated substrate temperature of 230°C. Comparison of the region illuminated by the laser (lower curve) to the unilluminated region (upper curve) is as expected for an "MBE-like" growth approach. In

⁶ R.L. Gunshor, L.A. Kolodziejski, A.V. Nurmikko, and N. Otsuka, "Molecular Beam Epitaxy of II-VI Semiconductor Microstructures," in *Semiconductors and SemiMetals*, ed. T.P. Pearsall (Boston: Academic Press, 1990).

particular, the growth rate is not increased, but slightly decreased when illuminated with photons. The resultant effect of the laser illumination is to tune the surface stoichiometry. The PL reflects the tuning of the stoichiometry by eliminating the weak donor-to-acceptor pair band luminescence which may be attributed to electron-to-acceptor-like vacancy recombination. The photoluminescence measurements provide additional information suggesting that the photon-assisted growth affects primarily the metalorganic Zn molecule and contributes to converting the DEZn into metallic Zn allowing incorporation into the crystalline lattice.

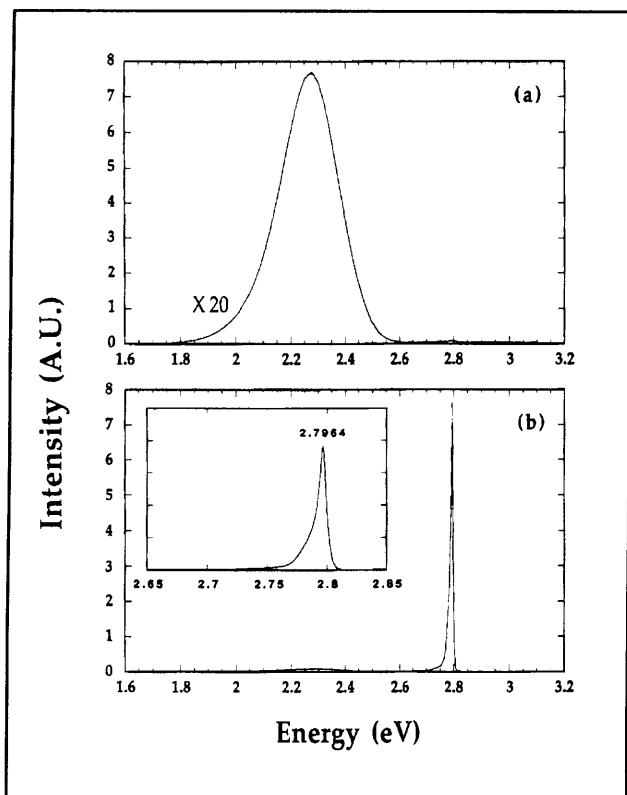


Figure 2. Photoluminescence of a ZnSe film grown using DEZn and DESe at a calibrated substrate temperature of 310°C (a) without laser illumination and (b) with $\lambda = 4579 \text{ \AA}$. Insert shows the energy of the dominant feature. Flow rates of 0.5 and 2.5 sccm were used for the DEZn and DESe, respectively.

3.3 Epitaxial Lattice-Matched III-V Buffer Layers for Wide Bandgap II-VI Visible Sources

Sponsors

Defense Advanced Research Projects Agency
Subcontract 216-25013
Joint Services Electronics Program
Contract DAAL03-92-C-0001

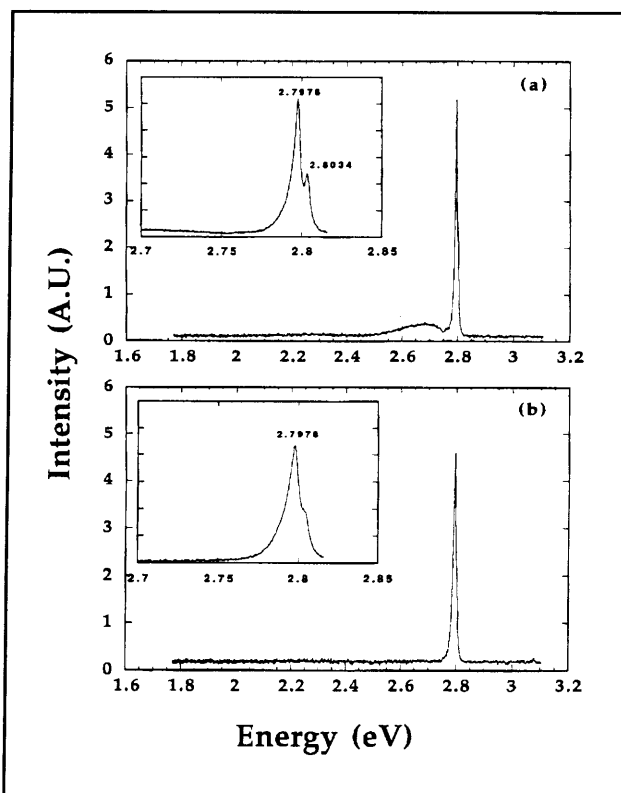


Figure 3. Photoluminescence of a ZnSe film grown using Zn and DESe (a) without laser illumination and (b) with $\lambda = 4579 \text{ \AA}$. Inserts show the energy of the dominant feature.

National Science Foundation
Grant DMR 92-02957

To take advantage of the numerous opportunities offered by long-lived, continuously operating, room temperature visible sources based on the wide bandgap II-VI semiconductors, several key technological barriers must be overcome. One very important difficulty is the lack of high quality II-VI substrate material. This particular limitation creates the need for the heteroepitaxy of II-VI layers onto III-V based substrates. If bulk substrates are employed, the only choice is to use GaAs which requires assessment of the effects of lattice mismatch (0.25%) strain on the resultant light emitting device (LED) structures. An additional consideration is the need for electronic confinement. Thus, the use of bandgap engineering and application of quantum wells is necessary for the design of the laser or LED device. Therefore, various II-VI ternary and quaternary layers are currently under investigation, with the resulting epilayer having a significantly varying lattice parameter. Issues of strain between both the substrate material and II-VI based active layer and between the well (narrow bandgap) and barrier (wider bandgap) II-VI alloy layers are crucial. The presence of strain contrib-

utes to the generation and propagation of defects which will ultimately affect the lifetime of any emitter.

Our interconnected epitaxy system provides the unique ability to investigate the growth of II-VI quantum well structures on III-V epitaxial surfaces where the lattice parameter ranges from that of GaP to InAs. These material systems cover the same lattice parameter range as Zn(S,Se,Te) and CdS, and all alloy combinations. The shaded region in figure 1 shows the range of lattice constants and energy bandgaps that can be grown in the CBE facility. We are presently investigating the growth of ZnSe on lattice-matched epitaxial (In,Ga)P buffer layers. As a first step, the growth conditions required to lattice match the (In,Ga)P to ZnSe are being determined. The epitaxial films are examined using double crystal x-ray diffraction and low temperature (10 K) photoluminescence. To date, the full width at half maximum (FWHM) of the (In,Ga)P peak (as determined by x-ray diffraction rocking curves) has been measured to be 34 arc seconds, whereas the GaAs substrate peak had a FWHM of 26 arc seconds. The photoluminescence spectra of the (In,Ga)P consists of a single peak corresponding to the near bandedge of the alloy. These (In,Ga)P films are typically grown at a substrate temperature of 470°C and with a growth rate between 0.25 and 1 μm per hour. Initial optical microscopy observations suggest that the starting surface morphology is featureless (unlike the cross-hatched surface of similarly strained (In,Ga)As which is typically used for buffer layers to ZnSe) and holds promise for the minimization of defect propagation into the active II-VI device layers and hence, enhancement of the performance of II-VI based optical sources.

3.4 Fabrication of Novel "Channel Dropping Filters" for Wavelength Division Multiplexed Photonic System Applications

Sponsor

Defense Advanced Research Projects Agency
Subcontract 542383

The fabrication of novel "channel dropping filters" for wavelength division multiplexed photonic system applications is currently underway. A channel dropping filter consists of three parallel, but coupled resonant waveguides, fabricated from (In,Ga)(As,P) to take advantage of the potential integration with the existing technology that is used in optical communication systems. The various (In,Ga)(As,P) layers

will be lattice-matched to InP substrates, but depending on the In and As mole fractions, will have various energy gaps and hence various indices of refraction. We are presently conducting experiments to determine the optimum growth conditions for the individual (In,Ga)(As,P) layers using in-situ reflection high energy electron diffraction, as well as ex-situ double crystal x-ray diffraction and photoluminescence. In addition, device simulations are underway to optimize the filter performance in order to determine (1) the appropriate mole fractions of quaternary layers necessary to vertically confine the optical signal, (2) the dimensions required to achieve the lateral waveguiding, and (3) the necessary coupling coefficient between the various waveguides. In this research program, a multi-investigator approach is required. Here, we will pursue the growth of the layered waveguide structure; the necessary gratings will be etched in the Submicron Structures Laboratory under the direction of Professor H.I. Smith (see part I, section 2, chapter 4), and the theory, device simulation, and measurements of filter performance are being carried out in the Optics and Devices Group with Professors H.A. Haus and E.P. Ippen (see part I, section 3, chapter 1).

3.5 Publications

Coronado, C.A., E. Ho, L.A. Kolodziejski, and C.A. Huber. "Photo-Assisted Molecular Beam Epitaxy of ZnSe." *Appl. Phys. Lett.* 61(5): 534-536 (1992).

Coronado, C.A., E. Ho, L.A. Kolodziejski, and C.A. Huber. "Laser-Assisted Growth of ZnSe by Metalorganic Molecular Beam Epitaxy." *Proceedings of the Material Research Society Symposium* 263: 181-186 (1992).

Coronado, C.A., E. Ho, and L.A. Kolodziejski. "Effect of Laser on MOMBE of ZnSe Using Gaseous and Solid Sources." *J. Cryst. Growth*. Forthcoming.

Ho, E., C.A. Coronado, and L.A. Kolodziejski. "Elimination of Surface Site Blockage due to Ethyl Species in MOMBE of ZnSe." *J. Electron. Mater.* Special Issue on Wide Bandgap II-VI Materials. Forthcoming.

Ho, E., C.A. Coronado, and L.A. Kolodziejski. "Photo-Assisted Chemical Beam Epitaxy of II-VI Semiconductors." *Proceedings of the Materials Research Society Symposium*, Boston, Massachusetts, November 28-December 4, 1992.