

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 8/10/95	3. REPORT TYPE AND DATES COVERED Final Technical 4/1/92 to 3/31/95	
4. TITLE AND SUBTITLE  Novel crystal growth of wide bandgap II-VI compounds for blue/green lasers by molecular beam epitaxy		5. FUNDING NUMBERS  ONR N00014-92-J-1541	
6. AUTHOR(S)  Wen I. Wang		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Electrical Engineering Department, Columbia University 500 West 120 Street, New York, NY 10027		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Office of Naval Research 800 N. Quincy Street, Arlington, VA 22217		11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release, distribution unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  P-type doping of ZnSe by nitrogen on off-axis substrate orientations resulted in carrier concentrations higher than that of the conventional (100) orientation. Low threshold current density lasers grown on (511)A operated at room temperatures have been achieved. Photoluminescence of (511) ZnMgSeS layers and CdZnSe quantum wells exhibited stronger luminescence intensity than the conventional (100) orientation, indicating that less defects were incorporated during crystal growth. Flip-chip transfer of ZnSeS/ZnSe/CdZnSe light-emitting diode films from GaAs substrates to Si substrates with improved quantum efficiencies was demonstrated.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED			16. PRICE CODE
18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

19960731 187

OFFICE OF NAVAL RESEARCH

FINAL TECHNICAL REPORT

FOR

1 April 1992 through 31 March 1995

\*\*\*\*\*

CONTRACT: N00014-92-J-1541

TITLE OF CONTRACT: Novel Crystal Growth of Wide Bandgap II-VI Compounds for Blue/Green Lasers by Molecular Beam Epitaxy

NAMES OF PRINCIPAL INVESTIGATORS: Wen I. Wang, Professor

NAME OF ORGANIZATION: Electrical Engineering Department, Columbia University

ADDRESS OF ORGANIZATION: Electrical Engineering Department, Columbia University, 500 West 120th Street, New York, N.Y. 10027

\*\*\*\*\*

Reproduction in whole, or in part, is permitted for any purpose of the University States Government.

This document has been approved for public release and sale: its distribution is unlimited.

The research performed under this contract started on April 1, 1992 and ended on March 31, 1995. The emphasis of our research under this program was to obtain high quality wide bandgap II-VI materials grown on novel crystal orientations for blue/green laser applications. Optimum crystal growth orientations (311 and 511) have been identified, p-type doping of ZnSe by nitrogen for off-axis substrate orientations resulted in carrier concentrations higher than that of the conventional (100) orientation, and low threshold current density lasers operated at room temperatures on (511)A orientation have been achieved. Band-structure calculations were carried out for various crystal orientations to help design quantum well structures. Photoluminescence of (511) epitaxial ZnSe, ZnMgSeS layers and CdZnSe quantum wells exhibited stronger luminescence intensity than the conventional (100) orientation, indicating that less defects were incorporated during crystal growth. n-type ZnTe has been obtained for the first time. Flip-chip transfer of ZnSeS/ZnSe/CdZnSe light-emitting diode films from GaAs substrates to Si substrates with improved quantum efficiencies was demonstrated. The achievements are summarized in the following:

### **Nitrogen doping and ohmic contacts to ZnSe and ZnTe on novel crystal orientations**

We used novel crystal orientations with favorable dangling bond configurations for acceptor site selection to improve p-type doping of ZnSe and ZnSe-based laser performance. The experimental work was guided by theoretical band structure calculations for the design of quantum well lasers.

Initially we performed the first comparison studies of N-doping of ZnSe for (100) and (311)A orientations. All previous molecular beam epitaxial (MBE) growth studies of ZnSe-based heterostructures used (100) orientation. In our approach, we used the (311)A orientation due to its large surface step density and preferred bonding configuration of the step-edge atom on A-face for acceptor site selection. (311) surface contains the highest surface step densities with monolayer step height, and the crystal growth occurs in the most favorable (100)-like growth mode. Our experimental results on N-doped ZnSe showed that with (100) and (311)A GaAs substrates mounted side-by-side under the same MBE growth conditions, while the p-type doping level is  $4 \times 10^{17} \text{ cm}^{-3}$  for (100), the doping concentration is  $1 \times 10^{18} \text{ cm}^{-3}$  for (311)A, i.e., more than two times higher than for (100). This result clearly indicated that the A-face has the beneficial effect for dopant site selection, as first proposed by us.

The influence of substrate orientation on the material properties of III-V compounds grown by MBE had been well-known, but all previous II-VI work used the conventional (100) orientation. By applying the III-V/II-VI analogy, we focused our efforts on surfaces with a high density of steps which are beneficial to crystal growth with minimum defects.

In our MBE growth, seven Knudsen effusion cells were used to provide the necessary elements for the II-VI epitaxy. Zn, Se, Mg, Te, and Cd are supplied in elementary form. ZnS powder was used as the sulfur source and  $\text{ZnI}_2$  were used to provide the iodine as the n-type dopant. All the sources are of 6N purity to exclude the effect of impurity. The p-type doping was provided by an Oxford Applied Research MPD-12 radical nitrogen gun. A  $(4 \times 2)$  Ga rich RHEED pattern appeared when the oxide was desorbed at  $580^\circ\text{C}$ . The substrate temperature was then lowered to  $240^\circ\text{C} \sim 300^\circ\text{C}$  for the subsequent growth. The RHEED pattern became streaky immediately after the growth initiated. The growth on off-axis yielded high quality materials. Low temperature PL spectrum of the nitrogen-doped ZnSe  $(311)\text{A}$  showed the dominant donor-to-acceptor peak at  $2.682\text{eV}$  and several phonon replicas indicative of high quality materials.

Wide bandgap II-VI compounds such as ZnSe and ZnS were also grown on elemental substrates such as Si and Ge to take advantage of the mature Si device technology for integrations with the II-VI light-emitting devices. We have achieved the growth of anti-phase domain free ZnS on Si substrates and ZnSe on Ge substrates for the first time. The use of Si and Ge substrates of  $(311)$  orientation was critical in that the  $(311)$  surface provides two distinctively different lattice sites: the single-dangling and the double-dangling bond sites. These two different lattice sites provide a natural selection mechanism for the Zn and Se adatoms. All previous studies of wide bandgap II-VI compounds such as ZnSe used the  $(100)$  orientation. We have obtained high quality ZnSe on Ge and ZnS on Si for the first time. The reflection high energy electron diffraction (RHEED) clearly showed an anti-phase domain free growth. The x-ray rocking curve demonstrated a full-widths-at-half-maximum (FWHM) as narrow as  $190$  arc seconds, which is the narrowest linewidth ever reported for ZnSe/Ge epitaxy.

In addition, we have investigated theoretically the orientation dependence of band structures for the II-VI quantum wells including ZnSe/ZnMgSeS based on the  $8 \times 8$  k-p model within the envelope function approximation. The in-plane effective mass for the first valence subband in the  $[111]$ -oriented quantum well is found to be the smallest among all orientations. We also found that the valence band structures display a large anisotropy for orientations such as  $[211]$ ,  $[311]$ , and  $[511]$  quantum wells, due to the different effective masses along the two in-plane directions. For quantum well lasers, the lighter dispersion mass will lead to a lower threshold current density. Our results indicated that the closer the orientation to the  $(111)$  pole, the lower the threshold current density. Our theoretical results should provide very useful guidelines for the design of ZnSe quantum well lasers.

Our doping results on the  $(311)\text{A}$  orientation can be expected to lead to improved p-n junctions for all the ZnSe-based structures due to the heavier p-type doping that can be

obtained. The ability to grow high quality single domain ZnS-on-Si and ZnSe-on-Ge means that the mature Si-based device technologies can be integrated with the II-VI light-emitting devices. Our theoretical modeling indicated that lower threshold current can be achieved on the (111) orientation than the conventionally used (100) orientation.

We achieved very heavy p-type doping in ZnTe: By carefully controlling the Zn/Te flux ratios, we were able to dope ZnTe p-type to  $8 \times 10^{19} \text{ cm}^{-3}$ . Specific contact resistance on our heavily p-type ZnTe is  $5 \times 10^{-5} \text{ ohm-cm}^2$ , which is suitable as ohmic contact for ZnSe-based devices.

The heavy p-type doping of ZnTe is expected to facilitate the formation of ohmic contacts for all ZnSe-based devices using the ZnSe/ZnTe graded contact scheme. The orientation dependence of sulfur incorporation is expected to improve the controllability of epitaxial layer structures.

We also experimented the growth of ZnSe with As-doping, and provided evidence that As can be a shallow p-type dopant: Arsenic has been proposed to be a deep acceptor in ZnSe when substituting Se site due to a large lattice relaxation, similar to the DX center in III-V's. However, based on the "covalent radius matching" rule, we expect simple substitutional As to be a shallow acceptor in ZnSe because its covalent radius matches well with that of Se. We have performed doping experiments using  $\text{Zn}_3\text{As}_2$  as the As doping source evaporated by a Knudsen effusion cell, and low temperature photoluminescence measurements unambiguously revealed that some of the As are being incorporated as shallow acceptors as evidenced by the existence of shallow acceptor bound excitons. The doping limitation at the present is limited by the amount of monomers that can be generated. However, with the improvement of plasma instruments, As monomers may well become available.

The ohmic contact of p-type ZnSe is difficult to obtain due to high Schottky barrier height (1.6V) and low doping concentration. To achieve high nitrogen doping in ZnSe, we found that low substrate temperature and low growth rate were essential. The samples with higher doping were grown at between  $240^\circ\text{C}$  and  $280^\circ\text{C}$ . It is believed to be caused by low sticking coefficient of nitrogen at high temperature. The growth rate was  $0.5 \mu\text{m/hr}$ . Lower temperature degraded the epi-layer quality, however ohmic contact is easier to form. Therefore, net acceptor concentrations,  $N_A - N_D$ , were determined using capacitance-voltage (C-V) profiling at 100 KHz. p-type GaAs substrates were used for the nitrogen doping experiment. 100  $\mu\text{m}$  diameter Cr/Au dot patterns were created using shadow mask. The thickness of Cr and Au is 20 nm and 100 nm, respectively. The residual In on the bottom of substrate was used for the back side ohmic contact. The I-V characteristics showed a good Schottky diode with more than 5V turn-on voltage.

The (511)A ZnSe were also experimented and showed a higher doping level than (100), consistent with the results on (311)A. The result of secondary-ion mass spectroscopy (SIMS) also indicated the enhanced nitrogen incorporation in these off-axis orientations.

Nitrogen-doped ZnTe on different orientations were also grown. ZnTe behaves differently from ZnSe in nitrogen doping. With the surface Fermi level pinned close to the valance band and high doping level, p-type ZnTe forms ohmic contact easily. All the samples were grown on semi-insulating GaAs substrates. The substrate temperature was between 250°C and 290°C under the Te-rich condition. The beam equivalent pressure (BEP) ratio of Te/Zn was about 2. A 0.5µm undoped AlSb was grown first in the III-V chamber. A 0.5µm undoped ZnTe buffer layer was then grown to prevent the parallel conduction at the interface and a 1µm ZnTe:N layer was grown on the top. Hall measurement was used to determine the doping concentration and mobility. The carrier concentration and mobility of the ZnTe on (100) GaAs substrate grown at the nitrogen background pressure of  $9 \times 10^{-7}$  Torr with 200W RF power, which is the same condition used to obtain  $1 \times 10^{18}$  cm<sup>-3</sup> doping level in ZnSe were in the mid- to high  $10^{19}$  cm<sup>-3</sup> range. The (311)B sample, with a record-high hole concentration, exhibits the highest hole concentration among all orientations.

We also tested the ohmic contact resistance formed by gold on our heavily doped (100) ZnTe. The transmission line pattern was used. The specific contact resistance, which is equal to the zero-length resistance multiplied by the contact area, of  $5 \times 10^{-5}$  Ω-cm<sup>2</sup> was obtained.

## Room Temperature Quantum Well Lasers Grown on (511) Orientation

According to recent laser and light emitting diode degradation studies by electroluminescence, stacking faults formed at the ZnSe/GaAs interface are the primary killers of the lasers. In order to improve the interface quality, we proposed an alternative orientation (511)A, which has been demonstrated to improve the interface quality of GaAs/AlGaAs quantum well, for growing high quality and reliable lasers. The motivation of using (511)A is that the higher step density will reduce the possibility of 3-dimensional nucleation, which can sepress the formation of stacking faults at the II-VI/III-V interface. The stronger PL intensity of (511)A ZnSSe and MgZnSSe also suggests better epi-layer quality, especially when higher Mg composition is needed.

The structure used for the SQW lasers grown in (511)A orientation was a separate confinement quantum well structure. The ZnSe<sub>x</sub>Te<sub>1-x</sub> pseudograded bandgap ternary layer was used for the contact layer to the p-type ZnSe. By taking the advantage of this contact layer, the threshold voltage has been reduced from more than 10V to 5.8V. A 5000Å Si doped GaAs buffer layer was first grown in the III-V chamber to provide good surface for the

following II-VI layers. The sample was then transferred into the II-VI chamber without the As coverage on the surface, which was reported to have a better interface. A thin ZnSe (200Å) was grown on the top of the GaAs before the growth of the laser structure. ZnI<sub>2</sub> was used to provide the n-type doping level more than  $1 \times 10^{19} \text{ cm}^{-3}$ . The substrate temperature was 260°C through out the whole structure. The temperature of the cells was carefully calibrated to precisely control the composition of each layer. The growth rate was 0.5 μm/hr for all the layers.

The broad area lasers were fabricated with the same procedure as the III-V lasers. Au was used for the top ohmic contact. A low turn-on voltage of 2.2 V indicates that Au and the graded ZnSe<sub>x</sub>Te<sub>1-x</sub> layer form a good ohmic contact to the quaternary cladding layer. Under low current injections, the I-V characteristic is exponential in form with an ideality factor of 2.05, implying the formation of a high quality p-n junction. The L-I curves of the laser bars with the cavity length of 750 μm showed threshold current density of 1000 A/cm<sup>2</sup>.

Room temperature lasing of ZnMgSeS/ZnSeS/CdZnTe/ZnSeS/ZnMgSeS quantum well lasers on (511)A orientation with a threshold current density of 1 kA/cm<sup>2</sup> was achieved. Most importantly, based on results of comparative studies of (100) and (511)A samples, the photoluminescence of (511)A samples always showed stronger and sharper emission peaks than their (100) counterparts, which indicated less defects are incorporated in the (511) epilayers and consequently a superior crystalline quality.

Our photoluminescence and quantum well laser results on the (511)A orientation indicated that more reliable lasers could be achieved in this orientation. We have discussed our results with researchers at 3M and Philips, and room temperature laser wafers were delivered to 3M for further studies. The heavy p-type doping of ZnTe is expected to facilitate the formation of ohmic contacts for all ZnSe-based devices using the ZnSe/ZnTe graded contact scheme.

In summary, we have investigated the influence of substrate orientation on the growth of II-VI compounds. Superior film quality and lasers were observed in the samples grown on (511)A substrates.

### **The 'Flip-Chip' Transfer of ZnSSe/ZnSe/CdZnSe LED Films**

A ZnSSe/ZnSe/CdZnSe light-emitting diode (LED) film grown on GaAs by molecular beam epitaxy has been successfully transferred from a GaAs substrate to a silicon substrate by combining both mechanical polishing and chemical wet etching techniques. The external quantum efficiency of the LED was enhanced by more than a factor of two via insertion of a reflector layer beneath the device structure. The device can be implemented in hybrid quasi-

monolithic integration. Technology applications include fabrication of LED's with enhanced external quantum efficiency and II-VI surface emitting lasers.

Thin film transfer technology has been shown to have applications in hybrid quasi-monolithic integration of dissimilar materials as well as in improving device performances (e. g. , the external quantum efficiency of LED's, the responsivity of metal-semiconductor-metal (MSM) detectors, etc.). There are two existing technologies used in thin-film transfer: epitaxial lift-off (ELO) and 'flip-chip' bonding. In the ELO technique, an epitaxial film, grown on an AlAs release layer, is undercut and lifted off of the growth substrate for transfer to the host substrate. The undercut and lift-off is accomplished by using diluted HF acid to selectively etch the AlAs layer (making use of the extremely high etching selectivity between AlAs and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x < 0.4$ )). In the flip-chip bonding technique, the original substrate is preferentially etched off without affecting the film quality by mounting the as-grown sample face-down on the host substrate. Relative ease-of-process and large area film transfer are advantages of the "flip-chip" bonding technique. A high quality etch-stop layer between the substrate and the device layer is required for the preferential etching to stop at the epitaxial layer. By using both the mechanical polishing and incorporating GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x=0.6$ ) etch-stop layers, we have for the first time successfully transferred a ZnSSe/ZnSe/CdZnSe green LED film from a GaAs substrate to a reflector-coated Si host substrate. The technology can be used in improving the external quantum efficiency of II-VI blue-green LED's and in the quasi-monolithic integration of II-VI devices with Si integrated circuits.

The LED structure consists of the following: 30nm n-ZnSe, a 1- $\mu\text{m}$  n-ZnS<sub>0.06</sub>Se<sub>0.94</sub> carrier confinement layer, 30nm undoped ZnSe, a 8nm undoped CdZnSe quantum well, 30nm undoped ZnSe, 30nm p-ZnSe, a 1 $\mu\text{m}$  p-ZnSSe upper confinement layer, a 50nm p-ZnSe<sub>x</sub>Te<sub>1-x</sub> pseudograded layer, and 100nm p-ZnTe contact.

The transfer process included: First, a 300nm Au film was deposited on the as-grown ZnTe surface as both metallic reflector and ohmic contact layer. The 1  $\text{cm}^2$  GaAs growth substrate was then polished to a thickness of 2.5 mils and mounted on a Au-deposited Si host substrate with conductive epoxy. The mechanical polishing process improves the quality of the transferred film as it considerably decreases the time for the GaAs substrate to be etched off. An etching process that is long in duration results in penetration of the etching solution through dislocations and defects in the substrate and etch-stop layer, thus deteriorating the quality of the LED film. The polished GaAs substrate was removed by a 25 minute application of  $\text{H}_2\text{O}_2(95\%)\text{-NH}_3(5\%)$  (by volume) solution. The etching stops at the AlGaAs layer due to the formation of a protective aluminum oxide film. Subsequent dipping of the sample in a 10% HF solution for several minutes removes the AlGaAs layer and aluminum oxide without etching the next GaAs layer. The remaining 400 nm GaAs layer was etched off by dipping the

sample in the  $\text{H}_2\text{O}_2(95\%)\text{-NH}_3(5\%)$  (by volume) solution for one second. This etching technique can also be used in fabricating mirrors for II-VI surface emitting lasers.

The exposed ZnSe layer can be visually distinguished from the GaAs film due to the color difference between ZnSe and GaAs. A Normarski micrograph of the ZnSe film after the GaAs substrate was etched off by the techniques described above is shown in Figure 2. For comparison purposes, part of the GaAs substrate edge (the darkest region in the micrograph) was protected by wax before the etching process. The morphology of the light area, the ZnSe layer, indicates an extremely smooth surface with no visible defects. The remaining AlGaAs film edge is between the dark and the light regions.

The LED's were defined by conventional optical lithography. Au was used as the n-type ZnSe ohmic contact metal. The typical spectrum of the LED exhibited a peak at 510nm. Device operation at 30mA revealed that there was no degradation in I-V characteristic after the film transfer. The enhancement of external quantum efficiency is attributed to the metallic reflector film beneath the devices. The external quantum efficiency of the transferred devices can be further improved by improving the material quality of the LED film and optimizing the device structure for photon recycling.

In summary, we have demonstrated the feasibility of the 'flip-chip' transfer technology for II-VI devices for the first time: we have successfully transferred a ZnSSe/ZnSe/CdZnSe LED film from a GaAs substrate to a Si substrate using the techniques of mechanical polishing and chemical etching. The device characteristics indicated no degradation after the transfer. The external quantum efficiency was increased by more than a factor of two due to the metallic reflector film beneath the devices. The technology has applications in hybrid quasi-monolithic integration, surface emitting laser fabrication, and LED external quantum efficiency enhancement.

## PUBLICATIONS AND PRESENTATIONS

- (1) W.I. Wang, "The problem of doping wide gap II-VI compound semiconductors and its solutions", Materials Research Society Proceedings vol. 228 "Materials for Optical Information Processing", pp. 319-325, 1992.
- (2) H. Xie and W.I. Wang, "Dependence of valence subband structures on substrate orientation in ZnSSe/ZnMgSSe quantum wells", J. Appl. Phys. 74, 1822-1825 (1993).

- (3) L.K. Li, Y. Wang, M. Jurkovic, and W.I. Wang, "Molecular beam epitaxial growth of single domain ZnSe on Ge", J. Appl. Phys. 75, 2026-2028 (1994).
- (4) W.I. Wang, "Doping of wide gap II-VI compound semiconductors grown by molecular beam epitaxy", presented at the ZnSe Workshop, Nov. 9, 1993, Hudson River Inn, Ossining, NY.
- (5) W.I. Wang, "Doping of ZnSe grown by molecular beam epitaxy", North American Conference on Molecular Beam Epitaxy, September 13, 1993, Stanford, CA.
- (6) L.K. Li, W.I. Wang, J.M. Gaines, J. Petruzzello, and T. Marshall, "Some doping results in ZnSe grown by molecular beam epitaxy", J. Vac. Sci. Tech. B12, 1197-1199 (1994).
- (7) I.W. Tao, M. Jurkovic, and W.I. Wang, "Doping of ZnTe by molecular beam epitaxy", Appl. Phys. Lett. 65, 1848-1849 (1994).
- (8) X. Li, I.W. Tao, and W.I. Wang, "Flip-chip transfer of ZnSSe/ZnSe/CdZnSe LED films", Electron. Lett. 31, 491-493 (1995).
- (9) I.W. Tao, Y. Wang, M. Jurkovic, and W.I. Wang, "ZnMgSeS/ZnSeS/CdZnSe strained quantum well lasers grown on (511)A", J. Vac. Sci. Tech. B13, 731 (1995).
- (10) I.W. Tao, Y. Wang, M. Jurkovic, and W.I. Wang, "ZnMgSeS/ZnS/CdZnSe strained quantum well lasers grown on (511)A orientation", J. Appl. Phys. 78, 2851 (1995).

#### PROFESSIONAL HONORS

W.I. Wang was elected IEEE Fellow for "contributions to compound semiconductor devices through innovative crystal growth", 1994.

W.I. Wang was a Member of Conference Committee, 21st Conference on Physics and Chemistry of Semiconductor Interfaces, Mohonk, New York, Jan 24-28, 1994.

W.I. Wang was Chairman of Program Committee for the 15th North American Conference on Molecular Beam Epitaxy to be held in September 1995 at the University of Maryland, College Park, MD.

#### PATENTS FILED

none