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PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Univ. of Illinois at Urbana-Champaign Urbana, IL 61801				
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13. ABSTRACT (Maximum 200 words)  Studies have been made of (1)  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs lasers on Si, (2) impurity induced layer disordering (which is an especially advantageous phenomenon in QWHs and SLs), (3) phonon-assisted laser operation and its unambiguous identification by control of the cavity Q of QWH samples, (4) the use of cavity Q to fill the recombination spectrum of  (continued on reverse side)				
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QWHs, (5) hydrolization and reliability of  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs and SLs, and (6) various other laser problems associated with higher gap crystals such as  $\text{In}_y(\text{Al}_x\text{Ga}_{1-x})_{1-y}\text{P}$ . The papers published in the time period of this report that have received substantial support from this project are listed as Refs. 1-10. Further work, which is to appear later, is listed as Refs. 11-15.

III-V SEMICONDUCTOR QUANTUM WELL LASERS AND  
RELATED OPTOELECTRONIC DEVICES ON SILICON

REPORT NO. 3

N. Holonyak, Jr./K. C. Hsieh/G. E. Stillman  
June, 1990

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Department of Electrical and Computer Engineering  
University of Illinois at Urbana-Champaign  
Urbana, IL 61801

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## I. INTRODUCTION

For some time (since 1976-77) we have been interested in III-V quantum well heterostructures (QWHs) and superlattices (SLs) and, in addition to fundamental effects, the special opportunities QWHs and SLs afford in making possible improved forms of lasers, not to mention other devices and optoelectronic systems. The prototype crystal materials and structures in these studies have been  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs and SLs grown on GaAs substrates. In spite of all the work that has been done in ten or more years on  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs and SLs, these particular QWHs and SLs continue to be of interest because of all of the fundamental and practical problems that can still be profitably considered. Also, in spite of the large lattice and thermal mismatch between  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  and Si, the possibility of splicing  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs on Si is of considerable interest, and even importance, assuming the mismatch defect generation, and thus high defect density, can be suppressed.

In the period covered by this report, ~~we have continued to study~~ <sup>studies have been made of:</sup> (1)  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  lasers on Si, (2) impurity induced layer disordering (which is an especially advantageous phenomenon in QWHs and SLs), (3) phonon-assisted laser operation and its unambiguous identification by control of the cavity Q of QWH samples, (4) the use of cavity Q to fill the recombination spectrum of QWHs, (5) hydrolization and reliability of  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs and SLs, and (6) various other laser problems associated with higher gap crystals such as  $\text{In}_y(\text{Al}_x\text{Ga}_{1-x})_{1-y}\text{P}$ . The papers published in the time period of this report that have received substantial support from this project are listed as Refs. 1-10. Further work, which is to appear later, is listed as Refs. 11-15.

*Quantum lasers, Silicon, etc. etc. etc.*

## II. QUANTUM WELL HETEROSTRUCTURE LASERS ON Si

It is now three years since we reported the first successful continuous wave (cw) room temperature (300 K) laser operation of  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs grown on Si. No other QWHs laser grown on Si have been operated cw 300 K with upright heat-sinking, i.e., with the Si itself serving as the heat sink and not the III-V QWH. This is important if, indeed, QWH lasers are ever to be integrated in arrays on Si and are to be capable of operation as individually addressable elements. In fact, our earlier work has shown that heat sinking via the Si substrate offers less thermal impedance and is an improvement over heat sinking via a GaAs substrate. If this were not the case, much of the interest in QWH lasers on Si would cease to exist since Si electronics could not be envisioned as supplying the drive signals for the QWH laser elements.

Because of the need (this Spring) for substantial maintenance and overhaul on our EMCORE metalorganic chemical vapor deposition (MOCVD) crystal growth reactor, followed by accidental Spring flood damage (with flood water steam damage to sensitive control circuits), and thus need now for more repair, we have not been able to pursue in this period further MOCVD QWH laser growth on TI GaAs-on-Si substrates. This is a serious delay, as we (Holonyak and Hsieh) have several experiments in progress to attempt reduction of mismatch dislocations in  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs grown on GaAs-on-Si substrates. We note that these experiments involve further exploitation of microcracks to relieve mismatch strain and reduce the dislocation density. We know from the success we have had in previous work that microcracks have played an important role in giving us cw 300 K QWH lasers on Si.

In fact, these are the only  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs on GaAs-on-Si (right-side-up diodes) to exhibit substantial cw 300 K laser operation ( $\sim 1$  day). These now are being operated (tested) further at lower temperatures to obtain a better understanding of mismatch dislocation and dark line defect generation, e.g., to ascertain whether these are driven by heat or by recombination radiation. These experiments are in progress (not yet complete or reportable), but have already yielded  $\sim 21$  day cw laser operation with the Si substrate held near 77 K. Because of the substantial thermal impedance of these lasers, which we have measured and reported earlier (JAP 64, 2854 (1988)), the QW active region itself is considerably hotter ( $\sim 200$  K). These results indicate QWH-on-Si laser diodes of significant performance capability (1-10 mW) are possible, but that problems with mismatch defects are still dominant. Nevertheless, further improvements should be possible.

### III. IMPURITY-INDUCED LAYER DISORDERING

The fact that impurity-induced layer disordering (IILD) is a powerful method to locally intermix (or globally intermix) QWH layers and shift the QWH from QW lower gap to bulk crystal higher gap provides an especially convenient method, based on normal integrated-circuit (IC) processing methods, to realize a wide variety of low-gap/high-gap device geometries. Among these are lasers, including now commercially available high performance IILD index-guided QWH lasers. From the initial work in Urbana (1980-81) IILD studies have now spread worldwide, to the point even of special workshops. Because of its importance, we obviously are continuing this area of work. Some of our more recent IILD work appears here as Refs. 1,3,4,6,7, and 8. Besides the

extension we have introduced of IILD by simultaneous Si-O diffusion in  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  and  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  QWHs, we have extended IILD studies to open tube rapid thermal annealing (RTA) procedures. This work will be reported later.

#### IV. PHONON-ASSISTED LASER OPERATION

Although phonon-assisted laser operation of photopumped QWHs, which are in the form of rectangular platelets and are free of contact and substrate layers, has been known since our initial work in 1978-79 (Holonyak and Kolbas), it has not been known until recently the extent to which this identification has depended on the cavity Q of the samples. We have shown that control of the sample Q, and selection of low-Q vs. high-Q photopumped laser operation, removes any ambiguity concerning observation of phonon-assisted laser operation. Some of our understanding of this problem is revealed in Ref. 5. The more interesting case of two-phonon laser operation is discussed in Ref. 10, and will soon be published. This area of work is continuing because of various unanswered questions about phonon involvement in QW laser operation.

Also, we are continuing our studies of control of sample Q (high-Q vs. low-Q) to influence recombination "mechanics" and behavior. For example, if a QWH sample is photopumped in a high Q configuration, then electron-hole pairs, photons, and phonons are maintained in and influence the recombination process. We are examining high Q photopumped QWH laser operation in order to see more of the recombination spectrum (which may eventually even be important practically for tunable laser sources).

## V. HYDROLIZATION AND RELIABILITY OF $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ QWHs

For a dozen years or more we have been working with QWHs and have been tracking the reliability of  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs, which will be recognized as the universal prototype QWH system. We have examined with greater or lesser success perhaps 1000 QWHs and SLs in 12 years, and find that a certain number of them hydrolize ("rust"). This appears to be an important reliability problem that is known in some quarters but which mainly is unknown and has been overlooked. (We know of at least one industrial concern that has experienced  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  reliability problems and has called for information and advice.) Some of our work on this problem has begun to be reported and appears here as Ref. 9, with a later paper to appear as Ref. 11. Since these are initial results, it is certain that more will be learned and published on oxygen contamination and attack of  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QWHs. This is apt to be a serious issue because of the usefulness and prevalence of the  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  heterostructure system.

## VI. OTHER LASER STUDIES

It is clear that even though  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  is an important heterostructure and QW system, in fact, is the prototype system, it is not without limitations and problems, and is not the only system of value and interest. For shorter wavelengths  $\text{In}_{1-x}\text{Ga}_x\text{P}$  is of particular interest, and its modification  $\text{In}_{1-y}(\text{Al}_x\text{Ga}_{1-x})_y\text{P}$ . Especially interesting is the case  $y \approx 0.51$  which matches GaAs, and offers other heterojunction and QWH possibilities. We have long experience with  $\text{In}_{1-x}\text{Ga}_x\text{P}$  (since 1970) and, with



Al substitution for Ga (e.g., just as the case  $\text{GaAs} \rightarrow \text{Al}_x\text{Ga}_{1-x}\text{As}$ ), we have extended our work to  $\text{In}_{0.5}(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{P}$ . Some of our recently submitted work on  $\text{In}_{1-y}(\text{Al}_x\text{Ga}_{1-x})_y\text{P}$  ( $y \sim 0.51$ ,  $x=0$  and  $y \sim 0.51$ , variable  $x$ ) is included here as Refs. 13 and 14. (We assume these reports will be published later.)

## VII. CONTRIBUTORS

The principal investigators contributing to various parts of the work reported here are:

- 1) N. Holonyak, Jr.
- 2) K. C. Hsieh
- 3) G. E. Stillman

(This report has been prepared by N. Holonyak, Jr.) The graduate students either receiving direct project support or otherwise contributing to various portions of the work reported here are:

- 1) J. M. Dallesasse, Ph.D. Student
- 2) D. C. Hall, Ph. D. Student
- 3) F. Kish, Ph.D. Student (A.T.&T. Fellowship)
- 4) J. S. Major, Jr., Ph. D. Student (Intel Fellowship, 1989-1990)
- 5) D. W. Nam, Ph. D. Student (Kodak Fellowship, Ph.D. completed, now at Spectra Diode Laboratories, San Jose, California).
- 6) A. R. Sugg, Ph.D. Student
- 7) E. J. Vesely, Ph. D. Student (NSF Fellowship)
- 8) T. A. Richard, Ph.D. Student
- 9) N. El-Zein, Ph.D. Student
- 10) M. Reis, Ph.D. Student

Note that some of the graduate students making contributions to this work (Refs. 1-15) have received support from other projects or have received fellowship support. Of the students listed above, Dallesasse, Hall, and Major are well into their doctoral research, and will finish their theses before the end of 1990. We mention that the National Science Foundation Engineering Research Center has supported much of our MOCVD crystal growth (EMCORE reactor), and our NSF MRL has supported our TEM and SIMS analyses, which are spread throughout much of the work reported here.

We mention also that since impurity-induced layer disordering (IILD) originated in Urbana, the University of Illinois holds a number of fundamental patents on this technology. In 1989 the first license agreement with an industrial laboratory (Spectra Diode Laboratories) for commercial use of IILD patents was concluded, and now it is likely that IILD technology will be more broadly licensed. (Licensing of IILD technology for the University of Illinois is actively being pursued by University Science, Engineering and Technology, Inc., 1465 Post Road East, P.O. Box 915, Westport, CT 06881.)

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# High Performance $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$ Quantum Well Lasers Defined by Silicon-Oxygen Impurity-Induced Layer Disordering

J. S. MAJOR, JR., L. J. GUIDO, N. HOLONYAK, JR., K. C. HSIEH, E. J. VESELY, D. W. NAM, D. C. HALL and J. E. BAKER

Electrical Engineering Research Laboratory,  
Center for Compound Semiconductor Microelectronics, and  
Materials Research Laboratory  
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

P. GAVRILOVIC, K. MEEHAN, W. STUTIUS and J. E. WILLIAMS

Polaroid Corporation, Cambridge, MA 02139

In these experiments impurity-induced layer disordering (IILD) utilizing chemical reduction of  $\text{SiO}_2$  by Al (from  $\text{Al}_{0.8}\text{Ga}_{0.2}\text{As}$ ) is employed to generate Si and O to effect layer disordering. The  $\text{SiO}_2\text{-Al}_{0.8}\text{Ga}_{0.2}\text{As}$  reaction is studied with respect to annealing ambient. By controlling the extent of disordering via  $\text{As}_4$  overpressure, closely spaced ( $\sim 1\text{ }\mu\text{m}$ ) Si-O IILD buried heterostructure lasers can be optically coupled or uncoupled. Direct observation of O incorporation into the buried layers is shown using secondary ion mass spectroscopy (SIMS). The thermal stability of separate-confinement  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  quantum well heterostructure (QWH) laser crystals is investigated using SIMS, transmission electron microscopy (TEM), and photoluminescence (PL) measurements. The data show that the thermal stability of a strained-layer  $\text{In}_{0.1}\text{Ga}_{0.9}\text{As}$  quantum well (QW) is strongly dependent upon: (1) the layer thickness and heterointerfaces of the  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs}$  waveguide layers located directly above and below the QW, (2) the type of surface encapsulant employed, and (3) the annealing ambient. Narrow single-stripe ( $< 2\text{ }\mu\text{m}$ ) lasers fabricated via Si-O diffusion and layer disordering exhibit low threshold currents ( $I_{\text{th}} \sim 4\text{ mA}$ ) and differential quantum efficiencies,  $\eta$ , of 22% per facet under continuous (cw) room-temperature operation.

**Key words:** InGaAs strained-layer laser, AlGaAs-GaAs-InGaAs quantum well heterostructure, impurity-induced layer disordering (IILD), Si-O IILD, coupled-stripe laser

## INTRODUCTION

Since the initial observation of continuous (cw) room-temperature (300 K) laser operation of strained-layer materials,<sup>1</sup> the study of pseudomorphic quantum well heterostructures (QWH's) for use in lasers and other optoelectronic devices has accelerated. Perhaps the most popular pseudomorphic heterosystem is simply that of a single  $\text{In}_x\text{Ga}_{1-x}\text{As}$  quantum well (QW) inserted into an  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs}$  QWH laser crystal. Strained layer lasers in the  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  system range from high power arrays, operating both with and without phasing-locking between elements, to low threshold single-stripe buried heterostructure laser diodes fabricated via Si-O impurity induced layer disordering (IILD).<sup>2-4</sup> This paper is concerned with the latter, specifically with two problems concerning buried heterostructures realized by Si-O IILD. The first is that of achieving a better understanding of the Al reduction of  $\text{SiO}_2$  for co-diffusion of Si and O into the QWH crystal to effect Si-O IILD.<sup>5,6</sup> The role of  $\text{As}_4$  overpressure during the anneal cycle and its effect on  $\text{SiO}_2$  reduction is ex-

amined, with attention given to controlling the total amount of layer disordering by varying the  $\text{As}_4$  overpressure. Second is that of determining the QWH parameters and conditions for a strained-layer heterostructure to be stable for extended annealing periods (i.e., when masked against Si-O IILD) at temperatures exceeding  $800^\circ\text{C}$ . Although theoretical work exists concerning the stability of strained-layer  $\text{In}_x\text{Ga}_{1-x}\text{As}$  QWH's, these models are not specifically targeted at the annealing conditions required to fabricate IILD buried heterostructure devices. Recently it has been shown that the thermal stability of a pseudomorphic  $\text{In}_x\text{Ga}_{1-x}\text{As}$  QW, surrounded top and bottom by GaAs, is improved by increasing the thickness of the GaAs overlayer from 200 to  $5000\text{ \AA}$ .<sup>7</sup> In this paper we consider the possibility that heterointerfaces within  $\sim 500\text{ \AA}$  of an  $\text{In}_x\text{Ga}_{1-x}\text{As}$  QW (buried beneath  $\sim 7000\text{ \AA}$  of  $\text{Al}_y\text{Ga}_{1-y}\text{As}$ ) have a major influence on the thermal stability of the strained-layer QW in an  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  QWH. In addition, by depositing different wafer encapsulants ( $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$ ) onto these crystals, we are able to alter the thermal stability of the strained-layer  $\text{In}_x\text{Ga}_{1-x}\text{As}$  QW. It is known that these two encapsulants ( $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$ ) create different populations of native defects that diffuse into the crystal and

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# Hydrogenated multiple stripe high-power long-wavelength (1.06 $\mu\text{m}$ ) continuous (10–50 $^{\circ}\text{C}$ ) $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$ quantum well heterostructure lasers

J. S. Major, Jr.,<sup>a)</sup> W. E. Plano, A. R. Sugg, D. C. Hall, N. Holonyak, Jr., and K. C. Hsieh

Electrical Engineering Research Laboratory, Center for Compound Semiconductor Microelectronics, and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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High-power operation of hydrogenated  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  ten-stripe arrays operating at  $\lambda \sim 1.06 \mu\text{m}$  is described. Continuous (cw) operation of arrays with uncoated facets that are stabilized in temperature at 10  $^{\circ}\text{C}$  has produced output powers as high as 375 mW/facet at 1.4 A. The optical coupling of the gain-guided arrays is shown to be significantly different from otherwise similar arrays fabricated in the  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs}$  system. Limited "lifetesting" (168 h) of these strained layer diodes, stabilized at 50  $^{\circ}\text{C}$  and a cw output power of 100 mW/facet (200 mW total), indicates good operating stability.

Since the initial demonstration of continuous (cw) room-temperature (300 K) stimulated emission from strained-layer  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  quantum well heterostructures (QWHs),<sup>1,2</sup> with wavelengths as long as 1.1  $\mu\text{m}$ ,<sup>2</sup> work has proceeded rapidly in the field of pseudomorphic laser device fabrication. Although the devices fabricated in this material system range from ridge waveguide lasers to broadband long-wavelength tunable sources,<sup>3–11</sup> little work has concentrated on the output capabilities of  $\text{In}_x\text{Ga}_{1-x}\text{As}$  quantum wells (QWs) near the critical thickness<sup>12,13</sup> under high-power operating conditions (cw 300 K), i.e., high power at longer wavelengths. In this letter we present data demonstrating both the high-power capability (750 mW total, cw) and stability of hydrogenated  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  QWH laser arrays operating at  $\lambda \sim 1.06 \mu\text{m}$ . In addition, we present data demonstrating different coupling behavior in these hydrogenated arrays than for similar arrays fabricated on  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs}$  QWH crystals.<sup>14</sup>

The epitaxial layers employed in this work have been grown using low-pressure metalorganic chemical vapor deposition (MOCVD)<sup>15</sup> in an Emcore GS3000-DFM reactor. The sources are ethyldimethylindium, trimethylgallium, trimethylaluminum, and arsine (100%). Carbon tetrachloride ( $\text{CCl}_4$ )<sup>16,17</sup> and hydrogen selenide are used for the  $p$ -type and  $n$ -type dopants, respectively. The growth temperature is 760  $^{\circ}\text{C}$  except for the QW region and the top GaAs contact layer. The  $\text{In}_x\text{Ga}_{1-x}\text{As}$  QW is grown at 630  $^{\circ}\text{C}$  to avoid desorption of In from the crystal surface, and the  $p$ -type GaAs contact layer is grown at 580  $^{\circ}\text{C}$  to enhance the incorporation of the C  $p$ -type dopant. The epitaxial layers are grown in the following order: (1) a 0.3  $\mu\text{m}$   $n$ -type ( $n_{\text{sc}} \sim 10^{18}/\text{cm}^3$ ) GaAs buffer layer, (2) a 0.15  $\mu\text{m}$   $n$ -type ( $n_{\text{sc}} \sim 10^{18}/\text{cm}^3$ )  $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$  buffer layer, (3) a 0.25  $\mu\text{m}$   $n$ -type ( $n_{\text{sc}} \sim 10^{18}/\text{cm}^3$ )  $\text{Al}_{0.40}\text{Ga}_{0.60}\text{As}$  layer, (4) a 0.9  $\mu\text{m}$   $n$ -type ( $n_{\text{sc}} \sim 5 \times 10^{17}/\text{cm}^3$ )  $\text{Al}_{0.30}\text{Ga}_{0.70}\text{As}$  lower confining layer, (5) an undoped 900  $\text{\AA}$   $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$  layer, (6) an undoped 600  $\text{\AA}$  GaAs layer with a 90  $\text{\AA}$  undoped  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  QW at its center, (7) an undoped 900  $\text{\AA}$

$\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$  layer, (8) a 0.9  $\mu\text{m}$   $p$ -type ( $n_{\text{c}} \sim 10^{18}/\text{cm}^3$ )  $\text{Al}_{0.50}\text{Ga}_{0.50}\text{As}$  upper confining layer, and (9) a 0.1  $\mu\text{m}$   $p$ -type ( $n_{\text{c}} \sim 3 \times 10^{19}/\text{cm}^3$ ) GaAs cap layer. The well size is determined by transmission electron microscopy (TEM), and the well alloy percentage is then calculated using the strain-corrected method described by Anderson *et al.*<sup>18</sup>

The laser fabrication process begins with the chemical vapor deposition of  $\sim 1000 \text{\AA}$  of  $\text{SiO}_2$  on the QWH crystal. The  $\text{SiO}_2$  is then patterned into stripes using standard photolithographic techniques. Two ten-stripe array geometries are used in this work. The first array pattern is 8- $\mu\text{m}$ -wide active stripes on 12  $\mu\text{m}$  centers and the second is 4  $\mu\text{m}$  active stripes on 12  $\mu\text{m}$  centers. After defining (masking) the stripes, we remove the GaAs cap with a calibrated  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$  (1:8:80) etch. The wafer is then exposed to a hydrogen plasma at a power of 600 W and a pressure of 1000 mTorr for 10 min.<sup>14</sup> After lapping and polishing to  $\sim 125 \mu\text{m}$ , we metalize the wafer using Ti-Pt-Au for the  $p$ -side contact and an evaporated and alloyed Au-Ge-Ni-Au contact for the  $n$ -type substrate side. The wafer is then cleaved into  $\sim 500\text{-}\mu\text{m}$ -wide bars, and individual dies are separated by sawing. These dies are mounted  $p$  down onto In-coated copper heat-sinks.

The array with the 8  $\mu\text{m}$  emitters on 12  $\mu\text{m}$  centers operates in a broad unstable twin-lobed pattern (data not shown), signifying some degree of out-of-phase coupling from emitter to adjacent emitter, which is in marked contrast to the well-defined stable twin-lobed pattern exhibited by hydrogenated arrays in the  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs}$  QWH system.<sup>14</sup> One possible explanation of this behavior is that since the emission energy of these lasers is much lower than otherwise similar  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs}$  QWH lasers, the recombination radiation experiences greatly reduced absorption. This causes unpumped regions of a gain-guided  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  QWH laser array to be more highly transmitting than the unpumped regions of an  $\text{Al}_y\text{Ga}_{1-y}\text{As-GaAs}$  QWH laser array. Thus, control of the coupling of the strained layer arrays can be improved by decreasing the stripe width to enhance single-mode operation within each stripe and by allowing greater distance between stripes to decrease transverse gain.<sup>19</sup>

<sup>a)</sup> Intel Doctoral Fellow.

# IMPURITY-INDUCED LAYER DISORDERING: CURRENT UNDERSTANDING AND AREAS FOR FUTURE INVESTIGATION

L.J. GUIDO\* and NICK HOLONYAK, JR.\*\*

\*Yale University, Department of Electrical Engineering, Center for Microelectronic Materials and Structures, P O Box 2157 Yale Station, New Haven, CT 06520

\*\*University of Illinois, Electrical Engineering Research Laboratory, Center for Compound Semiconductor Microelectronics, and Materials Research Laboratory, Urbana, IL 61801

## ABSTRACT

The purpose of this work is to give an overview of the current phenomenological understanding of impurity-induced layer disordering (IILD). First, we identify key experimental findings such as the influence of the crystal surface-ambient interaction, the Fermi-level effect, and the impurity concentration on Al-Ga interdiffusion. Second, we review the strengths and weaknesses of existing IILD models in consideration of the above mentioned experimental data. Finally, we discuss the pitfalls involved in generalizing the results of individual Al-Ga interdiffusion experiments in order to explain a broader collection of IILD data.

## INTRODUCTION

Because of the importance of high-temperature processes in semiconductor device fabrication the self-diffusion of host crystal atoms, e.g., in bulk Ge [1] and GaAs [2], has been studied previously to better understand the mechanisms of impurity diffusion. The recent interest in self-diffusion or interdiffusion phenomena in III-V semiconductors has been stimulated by advances in the epitaxial growth of quantum well heterostructure (QWH) crystals. Growth techniques such as metal organic chemical vapor deposition allow the device designer to replace homojunctions with heterojunctions and thick active layers with quantum wells to improve device performance. In many cases the key to realizing improved device performance is to maintain the as-grown heterointerface abruptness during subsequent high-temperature processing.

The first study of Al-Ga interdiffusion by Chang and Koma [3] focused on the effects of high-temperature As-rich annealing on heterointerface abruptness. The experiment involved a series of GaAs-AlGaAs-GaAs sandwich structures with relatively thick ( $\geq 1000\text{\AA}$ ) undoped epitaxial layers. Post-annealing auger electron spectroscopy (AES) analysis showed that the Al-Ga interdiffusion coefficient ( $D_{\text{Al-Ga}}$ ) is relatively small and



# Column III-column V sublattice interaction via Zn and Si impurity-induced layer disordering of $^{13}\text{C}$ -doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs superlattices

L. J. Guido,<sup>a)</sup> J. S. Major, Jr.,<sup>b)</sup> J. E. Baker, N. Holonyak, Jr., B. T. Cunningham, and G. E. Stillman

*Electrical Engineering Research Laboratory, Center for Compound Semiconductor Microelectronics, and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

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Experiments are described employing secondary-ion mass spectroscopy (SIMS) to study the stability of  $^{13}\text{C}$ -doped  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ -GaAs superlattices against Zn and Si impurity-induced layer disordering (IILD). The modulation depth of the SIMS  $^{27}\text{Al}$  and  $^{13}\text{C}$  signals is used as a sensitive probe of column III and column V sublattice interdiffusion. The data show that  $\text{C}_{\text{As}}$  is much more stable against Zn and Si IILD than the column III superlattice host crystal itself. The minor enhancement of  $\text{C}_{\text{As}}$  diffusion via the column III disordering agents, which is present to a significant extent for Si IILD but almost nonexistent for Zn IILD, suggests that there is no direct interchange of column III and column V sublattice atoms. The Zn and Si enhancement of carbon diffusion is probably caused by local Coulombic interaction between the diffusing  $\text{Zn}_i^+$  and  $\text{Si}_{\text{III}}^-$  species and the  $\text{C}_{\text{As}}$  acceptor.

Previous reports of optimized metalorganic chemical vapor deposition (MOCVD) for the growth of high-performance carbon-doped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum well heterostructure (QWH) lasers,<sup>1</sup> and for similar QWHs doped via an independently controllable carbon doping source ( $\text{CCl}_4$ )<sup>2</sup> show that the As sublattice acceptor carbon ( $\text{C}_{\text{As}}$ ) is perhaps one of the better  $p$ -type dopants for device use. These results are of interest not simply because carbon can be added to the existing selection of  $p$ -type dopants, but more importantly because carbon exhibits characteristics of an ideal dopant (see Refs. 1-3).

Earlier work on GaAs epitaxial crystals with  $\sim 1000 \text{ \AA}$   $^{13}\text{C}$  doping spikes has demonstrated that during post-growth thermal annealing carbon diffusion is very slow, and is relatively independent of the surface encapsulant and the annealing ambient.<sup>3</sup> Subsequent layer disordering experiments on  $^{13}\text{C}$ -doped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs QWH crystals have shown that such heterostructures are even more stable against high-temperature annealing than the corresponding undoped QWH crystals.<sup>4</sup> These results suggest that the  $\text{C}_{\text{As}}$  impurity influences Al-Ga interdiffusion on the column III sublattice. In the work described here, we use secondary-ion mass spectroscopy (SIMS) to explore the high-temperature stability of  $^{13}\text{C}$ -doped  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ -GaAs superlattices (SL) with  $^{13}\text{C}$  doping either in the barriers or in the wells. These QWH crystals are particularly suited for study of the column III-column V interaction, because diffusion on the As sublattice can be tracked via the SIMS  $^{13}\text{C}$  signal without introducing an additional strain energy variable. The data show that  $^{13}\text{C}$  doping spikes are more stable against Zn or Si impurity-induced layer disordering (IILD) than the superlattice host crystal itself. However, there is a significant interaction between the column III disordering agents, Zn and Si, and the As sublattice.

The QWH crystals used in this work have been grown by MOCVD in an Emcore GS3000-DFM reactor using the precursors trimethylgallium  $[(\text{CH}_3)_3\text{Ga}]$ , trimethylaluminum  $[(\text{CH}_3)_3\text{Al}]$ , and arsine (100%). The carbon doping source is 99%  $^{13}\text{C}$  enriched carbon tetrachloride ( $^{13}\text{CCl}_4$ ) diluted to 500 ppm in ultra-high purity  $\text{H}_2$ . The  $^{13}\text{C}$  isotope has been used to differentiate intentional carbon doping from the considerable  $^{12}\text{C}$  background that exists in MOCVD-grown  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ .<sup>5</sup> The MOCVD growth conditions are a growth rate of  $\sim 500 \text{ \AA min}^{-1}$ ,  $\text{AsH}_3$  flow  $\sim 100 \text{ sccm}$ , total  $\text{H}_2$  flow  $\sim 9 \text{ slm}$ ,  $T_G \sim 650^\circ\text{C}$ ,  $p_G \sim 100 \text{ Torr}$ , and a substrate rotation rate of  $\sim 1500 \text{ rpm}$ . The  $^{13}\text{CCl}_4$  flow is fixed at  $\sim 100 \text{ sccm}$  for each  $^{13}\text{C}$ -doped layer, resulting in a hole concentration of  $p_C \sim 10^{18} \text{ cm}^{-3}$ . The basic QWH crystal consists of an undoped  $\sim 2500 \text{ \AA}$  GaAs buffer layer grown on a Si-doped (100) GaAs substrate, followed by a 100-period  $^{13}\text{C}$ -doped  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ -GaAs SL ( $L_x \approx L_B \sim 250 \text{ \AA}$ ). The SL is confined symmetrically on top and bottom by a pair of  $\sim 2000 \text{ \AA}$   $^{13}\text{C}$ -doped layers of  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ . The upper  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$  confining layer is further capped by a  $\sim 1000 \text{ \AA}$  layer of  $^{13}\text{C}$ -doped GaAs. The two QWH crystals of interest here differ only in the SL doping; either the GaAs wells or the  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$  barriers are  $^{13}\text{C}$  doped.

The QWH crystals are prepared for thermal annealing by degreasing in organic solvents followed by  $e$ -beam deposition of  $\sim 300 \text{ \AA}$  of elemental Si as a source layer for the Si IILD case. For high-temperature annealing, one sample with and one without a Si diffusion source layer are loaded into a quartz ampoule along with a piece of solid As ( $\sim 15 \text{ mg}$ ). The ampoule is evacuated to  $10^{-6} \text{ Torr}$  and sealed to give a final volume of  $\sim 3 \text{ cm}^3$ . The two crystals are then annealed at  $825^\circ\text{C}$  for 24 h. The sample preparation for Zn IILD is identical except that  $\text{ZnAs}_2$  ( $\sim 5 \text{ mg}$ ) is used to provide the Zn and the excess As overpressures, and the annealing temperature is  $600^\circ\text{C}$  (3 h). After annealing the crystals are transferred to a high-vacuum SIMS chamber for analysis under identical vacuum conditions. The SIMS mea-

<sup>a)</sup> Now at Yale University, Department of Electrical Engineering, Center for Microelectronic Materials, and Structures, Box 2157 Yale Station, New Haven, CT 06520.

<sup>b)</sup> Intel Doctoral Fellow.

## Photopumping of Quantum Well Heterostructures at High or Low $Q$ : Phonon-Assisted Laser Operation

N. Holonyak, Jr.,\* D. W. Nam,<sup>†</sup> W. E. Plano, K. C. Hsieh,

Electrical Engineering Research Laboratory, Center for Compound Semiconductor Microelectronics, and  
 Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

and R. D. Dupuis<sup>‡</sup>

AT&T Bell Laboratories, Murray Hill, New Jersey 07974 (Received: April 28, 1989)

Data are presented showing the basic difference in the stimulated emission spectrum of a photopumped  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  or  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs-In}_x\text{Ga}_{1-x}\text{As}$  quantum well heterostructure (QWH) heat sunk in a high- $Q$  versus a low- $Q$  cavity configuration. In the high- $Q$  case a 1–2  $\mu\text{m}$  thick narrow (25–50  $\mu\text{m}$ ) cleaved rectangle, with the (100) GaAs substrate removed, is heat sunk compressed in In under a sapphire, giving a high cavity photon lifetime because of metal reflectors folded up along the four sample edges. In the latter case (low  $Q$ ) the (100) QWH rectangle is clamped under a sapphire into simple contact with Au, leaving the four cleaved {110} sample edges lossy and yielding, compared to carrier thermalization times, a short resonator photon lifetime across the sample. For photopumping (77 K,  $\text{Ar}^+$  laser, 5145 Å) of a low- $Q$  QWH sample, only lower energy recombination radiation is observed, including phonon-assisted laser operation (provided that the QWH is designed with good carrier, phonon, and photon confinement and with low alloy composition  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  thermalization layers generating GaAs-like phonons near the QW). For photopumping of an otherwise similar QWH heat sunk in the high- $Q$  configuration (long photon lifetime across the sample), recombination at higher energy can compete with carrier thermalization, and laser operation is observed on the confined-particle transitions, thus making unambiguous the identification of phonon sideband laser operation. Comparison of various QWHs heat sunk in the form of low- $Q$  or high- $Q$  resonators reveals the heterostructure layer configurations appropriate for phonon-assisted laser operation.

### Introduction

Ever since the transistor,<sup>1</sup> interest in semiconductors and their optical properties has grown. Fundamental to a semiconductor is its energy gap, an electron-hole energy gap that ensures interesting optical properties. We mention that in the "beginning" it was not known whether Ge (the first transistor material) was direct gap or, as it happened to be, indirect gap,<sup>2</sup> which, indeed, proved to be vital for the relatively long carrier lifetimes making possible the first bipolar transistors.<sup>1</sup> It is interesting to note that the distinction between a direct gap and an indirect energy gap was not lost on some of the earlier workers who considered using recombination radiation to achieve stimulated emission in a semiconductor.<sup>3,4</sup> The importance of this for semiconductor lasers became quite apparent later.<sup>5–8</sup> Immediately with the synthesis and discovery of the semiconductor behavior of III–V compounds,<sup>9</sup> direct-gap materials became available, and thus, if not initially that different in electrical properties than, say, Ge, they indeed proved to be different in optical properties. It is the direct-bandgap III–V compounds that lie at the heart of optoelectronics and, because they support stimulated emission (stimulated recombination radiation), are of concern here.

The difference between direct- and indirect-gap semiconductors is apparent in absorption measurements, and even more so in photoluminescence measurements, which, indeed, prove to be one of the simpler and more convenient methods of assessing semiconductor optical properties. This is particularly important for III–V semiconductors because of their strong light-emitting properties,<sup>10</sup> not to mention the fact that they serve as the basis for heterojunctions and quantum well heterostructures. Photoluminescence, or at higher levels, photopumping, has the advantage that experimental samples may be homogeneous or of the form of sophisticated heterostructures or may be doped or undoped. The latter is important in fundamental studies where the complications of doping impurities are not desired. In addition, photopumping has the further advantage that, without the need of assembling complicated devices, device behavior can often be determined or at least approximated.

In this paper we show, in photopumping experiments on quantum well heterostructures (QWHs), the importance of the experimental sample edge condition, i.e., whether it is naturally reflecting ( $\sim 30\%$ ) or made almost fully reflecting and thus whether the QWH sample is a low- $Q$  or a high- $Q$  active (photopumped) dielectric "slab". In Figure 1 we show compressed into an In (or Au) heat sink<sup>11</sup> a cleaved (100) QWH rectangle (substrate removed) with all four {110} cleaved edges imbedded and reflecting (high- $Q$  sample). For photopumping at low  $Q$  we use a sapphire to clamp the QWH sample into simple contact with the heat sink. For a sample fully pumped across its width in the high- $Q$  configuration (Figure 1), laser operation with widely spaced modes is observed across the sample on confined-particle transitions ( $\hbar\omega \approx E_{nn}$ ). In contrast, laser operation along the partially pumped sample length (narrowly spaced modes) is observed with

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(2) Bardeen, J. *Optoelectron.-Devices Technol.* 1987, 2, 124.

(3) Von Neumann, J. *IEEE J. Quantum Electron.* 1987, QE-23, 659. See also the J. V. N. letter to E. Teller (p 671).

(4) In 1962 J. Bardeen mentioned to one of us (N.H.) that several years earlier he had considered this same possibility for a student Ph.D. dissertation (i.e., stimulated emission in a direct semiconductor) but was not familiar at the time with the most prospective direct-gap material to suggest for the study. See: Holonyak, Jr., N. *IEEE J. Quantum Electron.* 1987, QE-23, 684.

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(9) We refer the reader to the interview with Alferov: Alferov, Zh. I. *Cradle of Soviet Physics. Priroda (Moscow)* 1988 (Nov), 4–11. Alferov (p 5) points out that in 1950 N. A. Goryunova and A. R. Regel (Leningrad) synthesized one of the III–V semiconductors and reported its properties at a meeting in Kiev. This report, and the fact that it revealed the III–V semiconductors, precluded the issuance of an English patent at a later date to H. Welker. Alferov points out that the work of Goryunova and Regel is not often cited because the proceedings of the Kiev meeting issued 2 years late (in *Izvestia-Academy of Sciences, U.S.S.R.*), and at that time Soviet journals were not regularly translated or followed in the West.

(10) This is true of direct-gap crystals and at least to some extent of indirect-gap materials such as GaP or  $\text{GaAs}_{1-x}\text{P}_x$  made quasi-direct by doping with an isoelectronic trap (N).

(11) Holonyak, Jr., N.; Scifres, D. R. *Rev. Sci. Instrum.* 1971, 42, 1885.

\* To whom correspondence should be addressed.

<sup>†</sup> Kodak doctoral fellow.

<sup>‡</sup> Work performed at Rockwell (Los Angeles).

## Al-Ga interdiffusion in heavily carbon-doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum well heterostructures

L. J. Guido, B. T. Cunningham, D. W. Nam,<sup>a)</sup> K. C. Hsieh, W. E. Plano, J. S. Major, Jr., E. J. Vesely,<sup>b)</sup> A. R. Sugg, N. Holonyak, Jr., and G. E. Stillman

*Electrical Engineering Research Laboratory, Center for Compound Semiconductor Microelectronics, and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

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Impurity-induced layer disordering experiments on  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum well heterostructures (QWHs) that are doped heavily with carbon are described. The data show that carbon doping retards Al-Ga interdiffusion relative to an undoped crystal, and that interdiffusion in C-doped QWHs is not enhanced by a Ga-rich (versus As-rich) annealing ambient. The data are inconsistent with most Fermi-level-effect models for layer disordering that do not include chemical impurity dependence or sublattice dependence, and that do not consider the possibility of inhibited Al-Ga interdiffusion in extrinsic crystals.

Recent studies of impurity-induced layer disordering (IILD) on  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum well heterostructures (QWHs) have identified the importance of the crystal surface interaction with the ambient and the so-called Fermi-level effect.<sup>1-3</sup> Despite these encouraging results there is little agreement yet on a specific model for layer disordering. One important issue that remains to be resolved is to what extent the column III and column V sublattices couple during interdiffusion. We have investigated these issues further via annealing studies on  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs QWHs that are doped with the As-sublattice acceptor carbon ( $\text{C}_{\text{As}}$ ). The two salient features of this work are that C-doped *p*-type

QWHs respond much differently to high-temperature annealing than more typical Mg-doped *p*-type QWHs, and that the  $\text{C}_{\text{As}}$  acceptor *inhibits* column-III sublattice layer disordering. These observations bring into question models for IILD that rely solely on the Fermi-level effect.

In order to determine the influence of the crystal surface stoichiometry on Al-Ga interdiffusion in a *p*-type crystal, a 40-period C-doped  $\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$ -GaAs superlattice ( $L_y, L_z \sim 250 \text{ \AA}$ ) has been annealed under Ga-rich (+ Ga), As-rich (+ As), or equilibrium GaAs vapor pressure (+ 0) conditions. The superlattice crystal has been grown by metalorganic chemical vapor deposition (MOCVD) in an Emcore GS3000-DFM reactor using trimethylgallium, trimethylaluminum, and arsine (100%) precursors. The carbon doping level is controlled independently using a source of 500 ppm  $\text{CCl}_4$  in ultrahigh purity

<sup>a)</sup> Kodak Ph.D. fellow.

<sup>b)</sup> National Science Foundation Ph.D. fellow.

# Layer disordering of *n*-type (Se) and *p*-type (C) $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs superlattices by S diffusion

J. S. Major, Jr.,<sup>a)</sup> J. M. Dallesasse, L. J. Guido,<sup>b)</sup> J. E. Baker, W. E. Plano,<sup>c)</sup>  
A. R. Sugg, E. J. Vesely,<sup>d)</sup> T. A. Richard, and N. Holonyak, Jr.

Electrical Engineering Research Laboratory, Center for Compound Semiconductor Microelectronics,  
and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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Data are presented showing limited layer disordering (or intermixing) of S-diffused Se-doped or C-doped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs superlattices. The S diffusion is characterized via secondary-ion mass spectroscopy, shallow angle beveled cross sections, and absorption measurements. Limited intermixing of column-III-site atoms ( $\text{Al}=\text{Ga}$ ) as well as minimal displacement of the column-V-site acceptor C is observed. The S diffusion depth is much greater than that of the layer disordering, the magnitude of which is similar to that of native-defect vacancy-assisted disordering (vacancy  $V_{\text{III}}$ ).

It is well known that the diffusion of Zn,<sup>1</sup> Si,<sup>2</sup> or Ge<sup>3</sup> causes impurity-induced layer disordering (IILD) of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum well heterostructures (QWHs). The donor S has also been studied as a disordering agent from both diffused<sup>4</sup> and implanted<sup>5,6</sup> sources. These reports<sup>4-6</sup> offer conflicting data about the capability of S to disorder  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs superlattices (SLs) and quantum well heterostructures (QWHs). We note that the choice of impurity species for IILD, and column III or column V atom intermixing, is important from both a technological and fundamental basis. Because of ambiguity in previous work and to avoid the issue of implantation damage and its possible role in disordering phenomena, we reexamine here S diffusion for layer disordering of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs QWHs or SLs. We present data on S diffusion in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs SLs showing that the magnitude of the layer disordering is only comparable to that of vacancy ( $V_{\text{III}}$ ) disordering.<sup>7</sup> As it is conceivable that the donor S could be a strong disordering agent of column-V-sublattice atoms in some forms of III-V heterostructures,<sup>8</sup> data are also presented showing that C (acceptor on a column V site) is not significantly displaced during S diffusion in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs SLs, thus suggesting that the effect of S diffusion on atom displacement in the column V sublattice is also minor.

The QWH crystals used in this work have been grown by metalorganic chemical vapor deposition (MOCVD) in an Emcore GS3000-DFM reactor using trimethylgallium, trimethylaluminum, and arsine (100%) as precursors. The source used for the <sup>13</sup>C doping is 99% <sup>13</sup>C-enriched carbon tetrachloride ( $\text{CCl}_4$ ;<sup>9</sup> at a concentration of 500 ppm in ultra-high purity  $\text{H}_2$ ). The first crystal used in this work, SL1, consists of an undoped 2500 Å GaAs buffer layer grown on a Si-doped (100) GaAs substrate, followed by a 100 period <sup>13</sup>C modulation-doped  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ -GaAs SL ( $L_x \approx L_y \approx 250$  Å). The superlattice is confined on top and bottom by  $\sim 2000$  Å <sup>13</sup>C-doped layers of  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ , with an  $\sim 1000$  Å layer of GaAs capping the upper  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$

confining layer. The  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$  SL barriers are doped  $\sim 10^{18} \text{ cm}^{-3}$  with <sup>13</sup>C, while the SL quantum wells are undoped. The second QWH crystal used in this work, SL2, is identical to SL1, except that it is uniformly doped with <sup>13</sup>C to a concentration of  $\sim 10^{18} \text{ cm}^{-3}$ . The third QWH crystal employed here, SL3, consists of a 2000 Å GaAs buffer layer followed by a 20 period  $\text{AlAs}$ -GaAs SL ( $L_x \approx L_y \approx 500$  Å). All epitaxial layers of SL3 are doped with Se from hydrogen selenide to a level of  $\sim 10^{18} \text{ cm}^{-3}$ .

The diffusion source used for these experiments is an 800 Å layer of GaS electron beam deposited onto a piece of GaAs. The diffusion source ( $\sim 5 \text{ mm} \times 5 \text{ mm}$ ) and SL samples are sealed in an evacuated quartz ampoule (volume  $\sim 3 \text{ cm}^3$ ) with elemental As (2–10 mg). For temperatures below 900 °C and excess As less than  $\sim 10 \text{ mg}$ , the SL surfaces are specular. At higher temperatures or As overpressures, however, surface reactions roughen the surface. The diffusion of S is characterized by capacitance-voltage (*C-V*) electrochemical-etch profiling of the diffused samples. The S profile is well modeled by the standard equation

$$C(x) = C_0 \operatorname{erfc}(x/2\sqrt{Dt}), \quad (1)$$

as previously reported.<sup>10,11</sup> For the conditions given here the diffusion coefficient into undoped GaAs is  $D_S \sim 3.1 \times 10^{-13} \text{ cm}^2/\text{s}$  (825 °C,  $\sim 2 \text{ mg}$  excess As).

To study the effect of S diffusion upon column-III atom intermixing ( $\text{Al}=\text{Ga}$ ) and simultaneously displacement of the column-V site acceptor C, SL1 has been diffused with S for 24 h at 825 °C with  $\sim 2 \text{ mg}$  of As in the anneal ampoule. The sample is coated by chemical vapor deposition (CVD) with  $\sim 1000$  Å of  $\text{Si}_3\text{N}_4$  and is patterned into 150 μm stripes on 500 μm centers using standard photolithographic techniques. In the regions covered with  $\text{Si}_3\text{N}_4$  no S diffusion occurs. In Fig. 1 secondary-ion mass spectroscopy (SIMS) data are shown for the <sup>27</sup>Al, <sup>13</sup>C, and <sup>32</sup>S signals for (a) bare and (b) masked portions of SL1. The data are obtained using a Cs<sup>+</sup> probe beam with the sample biased to collect negative secondary ions. The vertical dashed lines of Figs. 1(a) and 1(b) show the <sup>13</sup>C doping as being in phase with the  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$  barriers. As seen in Fig. 1(a), S has diffused through the  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$  upper cladding layer (0.1 to 0.3 μm) and through the layers sampled by the SIMS mea-

<sup>a)</sup> Intel Fellow.

<sup>b)</sup> Now at Yale, New Haven, CT.

<sup>c)</sup> Now at Spectra Diode Labs., San Jose, CA.

<sup>d)</sup> National Science Foundation Fellow.

# Column III vacancy- and impurity-induced layer disordering of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs heterostructures with $\text{SiO}_2$ or $\text{Si}_3\text{N}_4$ diffusion sources

L. J. Guido,<sup>a)</sup> J. S. Major, Jr.,<sup>b)</sup> J. E. Baker, W. E. Plano, N. Holonyak, Jr., and K. C. Hsieh

*Electrical Engineering Research Laboratory, Center for Compound Semiconductor Microelectronics, and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

R. D. Burnham

*Amoco Technology Company, Amoco Research Center, Naperville, Illinois 60566*

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Experiments are described determining the critical parameters for vacancy- and impurity-induced layer disordering of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum-well heterostructure (QWH) crystals that utilize  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  diffusion source layers. The  $\text{SiO}_2$ - or  $\text{Si}_3\text{N}_4$ -capped QWH crystal surface reaches equilibrium with the external annealing ambient by diffusion of Ga and As through the encapsulant layer, thus determining the crystal-surface deviation from stoichiometry and the column III vacancy concentration for layer disordering. By proper design of the QWH crystal, encapsulant layer thickness, and annealing ambient, the  $\text{SiO}_2$  ( $\text{Si}_3\text{N}_4$ ) can be employed as a column III vacancy source (or mask) or as a Si and O (or N) diffusion source to effect impurity-induced layer disordering.

## I. INTRODUCTION

Dielectric layers (e.g.,  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$ ) have long been used passively in *III-V* semiconductor-device-fabrication technology for high-temperature crystal surface encapsulation, diffusion masking, and patterned optical waveguides. Recent work on heterosystems such as  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs has shown that  $\text{SiO}_2$  can be employed in an active role for optoelectronic device fabrication via vacancy- and impurity-induced layer disordering.<sup>1-3</sup> For example, buried heterostructure lasers have been fabricated by encapsulating (selectively) an  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum-well heterostructure (QWH) crystal with patterned  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$ , and then annealing the crystal at high temperature.<sup>1</sup> The  $\text{SiO}_2$  is porous to Ga diffusion (out-diffusion) and thus provides column III vacancies for layer disordering. Alternatively, the GaAs cap itself has been patterned (wet etched) and the underlying high-gap  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  layer is then contacted directly by  $\text{SiO}_2$ .<sup>4</sup> During high-temperature annealing the  $\text{SiO}_2$  is reduced by Al, thus supplying Si and O for impurity-induced layer disordering (IILD).

In the experiments described in this work we extend the earlier work using secondary-ion-mass spectroscopy (SIMS), Nomarski-contrast optical microscopy, and shallow-angle beveling to study the high-temperature stability of  $\text{SiO}_2$ -GaAs,  $\text{SiO}_2$ - $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$ , and  $\text{Si}_3\text{N}_4$ - $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$  interfaces. The data show that the intended device applications dictate the appropriate choice of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs QWH crystal, encapsulant layers, and annealing conditions. For example, if slight vacancy-induced disordering is desired to simply modify the QWH band edge, the following steps must be taken to insure  $\text{SiO}_2$ -QWH crystal interface

stability: (1) The  $\text{SiO}_2$  layer must be thick and pinhole-free, and (2) the QWH crystal must have a relatively thick GaAs cap layer to prevent indirect Al- $\text{SiO}_2$  interaction via layer disordering. In contrast, if more selective and complete IILD is desired, the Al- $\text{SiO}_2$  reduction reaction must be assisted by: (1) reducing the  $\text{SiO}_2$  thickness; (2) employing a thin GaAs cap layer to prevent oxidation of the  $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$ ; and (3) using a large  $\text{As}_4$  overpressure for annealing. In addition, the data demonstrate that of the various choices considered the  $\text{Si}_3\text{N}_4$ -QWH crystal interface is the most stable, because  $\text{Si}_3\text{N}_4$  is generally pinhole-free and not particularly porous to Al, Ga, or As. Nevertheless,  $\text{Si}_3\text{N}_4$  can be used for Si and N diffusion and thus for IILD via the  $\text{Si}_3\text{N}_4$ -Al reduction reaction.

## II. EXPERIMENT

The  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs QWH crystals used in this work have been grown by metalorganic chemical vapor deposition (MOCVD) in an Emcore GS3000-DFM vertical-flow reactor and, in the case of one superlattice crystal, in a home-built vertical-flow reactor. Two of the QWH crystals (LG1220, LG1232) consist of an undoped GaAs buffer layer ( $\sim 2000 \text{ \AA}$ ) grown on a Cr-doped (100) GaAs substrate, followed by a  $\sim 2\text{-}\mu\text{m}$  layer of Mg-doped  $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$  ( $\rho_{\text{Mg}} \sim 7 \times 10^{17} \text{ cm}^{-3}$ ). The high-gap  $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$  layer is further capped by a thin undoped GaAs layer ( $\sim 600 \text{ \AA}$ ) to form the single GaAs- $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$  heterointerface that is of interest. The growth conditions for the single-heterostructure crystal LG1220 are a growth rate of  $\sim 2000 \text{ \AA min}^{-1}$ ,  $\text{AsH}_3$  (100%) flow  $\sim 180 \text{ sccm}$ , total  $\text{H}_2$  flow  $\sim 8 \text{ slm}$ ,  $T_G \sim 760^\circ\text{C}$ ,  $p_G \sim 150 \text{ Torr}$ , and substrate rotation rate of  $\sim 1500 \text{ rpm}$ . The growth conditions for crystal LG1232 are identical except that  $T_G \sim 825^\circ\text{C}$ . The superlattice crystal is nominally undoped and consists of a GaAs buffer layer ( $\sim 2000 \text{ \AA}$ ), a  $\sim 1\text{-}\mu\text{m}$   $\text{Al}_{0.60}\text{Ga}_{0.40}\text{As}$  etch-stop layer, followed by a second GaAs buffer layer ( $\sim 0.5 \text{ }\mu\text{m}$ ), and finally

<sup>a)</sup> Now at Yale University, Department of Electrical Engineering, Center for Microelectronic Materials and Structures, Box 2157 Yale Station, New Haven, CT 06520.

<sup>b)</sup> Intel Doctoral Fellow.

# Stability of AlAs in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -AlAs-GaAs quantum well heterostructures

J. M. Dallesasse, P. Gavrilovic,<sup>a)</sup> N. Holonyak, Jr., R. W. Kaliski,<sup>b)</sup> D. W. Nam,<sup>c)</sup> and E. J. Vesely<sup>d)</sup>

*Electrical Engineering Research Laboratory, Center for Compound Semiconductor Microelectronics, and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

R. D. Burnham

*Amoco Technology Company, Amoco Research Center, Naperville, Illinois 60566*

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Data are presented on the long-term ( $\geq 8$  yr) degradation of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -AlAs-GaAs quantum well heterostructure material because of the instability of underlying (internal) AlAs layers. Material containing thicker ( $> 0.4 \mu\text{m}$ ) AlAs "buried" layers (confining layers) is found to be much less stable than material containing thinner ( $\leq 200 \text{ \AA}$ ) AlAs layers. Hydrolysis of the AlAs layers because of cleaved edges and pinholes in the cap layers leads to the deterioration.

Since the introduction of AlAs barrier layers in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum well heterostructures (QWHs) to suppress the effects of alloy clustering,<sup>1</sup> the use of AlAs layers in QWHs has become quite common in lasers and other devices. It is of interest that almost from the beginning of extensive study of III-V compounds the binary Al-bearing III-V's have been listed as unstable.<sup>2</sup> In early work on high-performance  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs solar cells, AlAs layers employed as window layers have been found to be unstable when exposed to air.<sup>3,4</sup> In order to circumvent this problem, AlAs layers have either been passivated using anodization,<sup>3</sup> or have been replaced by high-composition ( $x \sim 0.8$ )  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  layers.<sup>4</sup> In QWHs they are, of course, "buried" in the layered structure. As is well known<sup>2</sup> the instability of AlAs is due to the extremely reactive nature of the Al, particularly in a moist environment. Because of this behavior, an important consideration for the reliable operation of QWH lasers, as well as other QWH devices, is the stability of the AlAs layers if they are employed in the QWH. In this letter data are presented on the degradation of AlAs in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -AlAs-GaAs QWHs and superlattices (SLs). Thicker ( $> 0.4 \mu\text{m}$ ) AlAs layers that are exposed to the environment through "pinholes" in encapsulating layers or at cleaved edges are found to decompose, resulting in a slow destruction of the QWH material. Thinner AlAs layers ( $< 200 \text{ \AA}$ ) contained within a SL structure are found to have increased stability.

The crystals used in this experiment are grown by metalorganic chemical vapor deposition (MOCVD) on {100} *n*-type GaAs substrates.<sup>5</sup> In Fig. 1(b) a scanning electron microscope (SEM) photomicrograph of the cross section of the primary QWH material used in this experiment is shown. Growth begins with a thick *n*-type GaAs buffer layer and then an  $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$  layer ( $\sim 0.8 \mu\text{m}$ ). This is followed by a  $\sim 0.4\text{-}\mu\text{m}$ -thick *n*-type AlAs lower confining layer. Next is the symmetrical active region of the QWH which

consists of a  $\sim 150 \text{ \AA}$  GaAs quantum well (QW) between two  $\sim 600 \text{ \AA}$   $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$  waveguide (WG) layers. Then a thick ( $\sim 0.5 \mu\text{m}$ ) AlAs *p*-type upper confining layer is grown, followed by the growth of a  $\sim 0.4 \mu\text{m}$  *p*-type  $\text{Al}_{0.75}\text{Ga}_{0.25}\text{As}$  layer. The entire structure is capped by a heavily doped *p*-type GaAs cap layer ( $\sim 0.6 \mu\text{m}$ ). The 40-period comparison SL sample is grown similarly by MOCVD but with  $150 \text{ \AA}$  AlAs barriers and  $45 \text{ \AA}$  GaAs wells.

The *p-n* QWH crystal of main issue here dates back to April, 1982. At the time of its growth unmounted probe tested laser diodes exhibited (300 K) pulsed threshold current densities of  $3000 \text{ A/cm}^2$ . This indicates fair quality crystal. The as-grown crystal was observed (by optical microscopy) to be free of any obvious defects. The wafer was then maintained under normal room environmental conditions. With the passage of time, atmospheric water vapor reacts with the buried AlAs layers, possibly forming  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{AlAs} \cdot 8\text{H}_2\text{O}$ ,  $\text{AlO}(\text{OH})$ , or  $\text{Al}(\text{OH})_3$ . This occurs via crystal edges and pinholes in the GaAs-Al $_x\text{Ga}_{1-x}\text{As}$  encapsulating layers, thus leading to slow decomposition of the QWH material. Two examples of the destructive reactions that can occur are

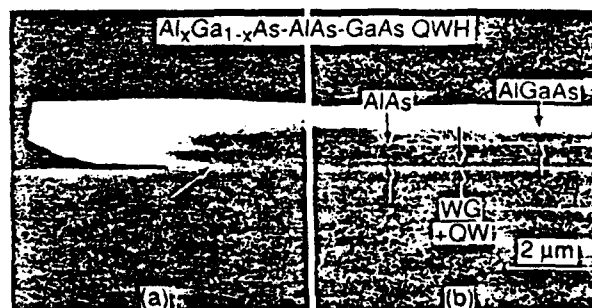


FIG. 1. Scanning electron microscope (SEM) photomicrograph of the cross section of an  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -AlAs-GaAs QWH grown in 1982 that, because of thick ( $\geq 0.4 \mu\text{m}$ ) "buried" AlAs confining layers and cleaved edges and pinholes, hydrolyzes and deteriorates. The arrow in (a) marks the boundary between hydrolyzed AlAs and AlAs that is unreacted. Panel (b) shows the layer structure of the as-grown QWH material in an area unaffected by the hydrolysis.

<sup>a)</sup> Now at Polaroid (Polaroid Corp., 21 Osborn St., Cambridge, MA 02139).

<sup>b)</sup> Now at Amoco (Amoco Research Center, Naperville, Illinois 60566).

<sup>c)</sup> Kodak Doctoral Fellow.

<sup>d)</sup> National Science Foundation Doctoral Fellow.

TWO-PHONON LASER OPERATION (4.2-77 K) OF PHOTOPUMPED

$\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  QUANTUM WELL HETEROSTRUCTURES

D. W. Nam,<sup>a)</sup> N. Holonyak, Jr., and E. J. Vesely<sup>b)</sup>

Electrical Engineering Research Laboratory,  
Center for Compound Semiconductor Microelectronics, and  
Materials Research Laboratory

University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

R. D. Dupuis

The University of Texas at Austin, Austin, TX 78712

ABSTRACT

Data are presented showing that photopumped  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  quantum well heterostructures (QWHs) are capable of stimulated emission (because of the large confined phonon population) one and two longitudinal optical (LO) phonons below the lowest confined-particle electron-to-heavy hole transition ( $\text{el} \rightarrow \text{hl}$ ). The phonon-assisted laser operation two phonons below the  $\text{el} \rightarrow \text{hl}$  transition ( $\Delta E = 2\hbar\omega_{\text{LO}} = 2 \times 36 \text{ meV}$ ) is identified unambiguously using (on a single sample) two types of heat sink configurations, high-Q to turn-on and low-Q to turn-off the stimulated emission on the  $\text{el} \rightarrow \text{hl}$  (reference) transition. Because the one- and the two-phonon laser operation (4.2 K) are spectrally very narrow, narrower than that on QW confined-particle transitions, their separation affords an accurate measurements of QW phonon energy ( $\hbar\omega_{\text{LO}} = 36.1 \text{ meV}$ ).

ENVIRONMENTAL DEGRADATION OF  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$   
QUANTUM-WELL HETEROSTRUCTURES

J. M. Dallesasse, N. El-Zein, N. Holonyak, Jr., and K. C. Hsieh

Electrical Engineering Research Laboratory,

Center for Compound Semiconductor Microelectronics, and

Materials Research Laboratory

University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

R. D. Burnham

Amoco Research & Development, Naperville, Illinois 60566

R. D. Dupuis

University of Texas at Austin, Austin, TX 78712

ABSTRACT

Data describing the deterioration of  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  heterostructures in long-term exposure (2 to 12 years) to normal room environmental conditions ( $\sim 20\text{-}25^\circ\text{C}$ , varying humidity) are presented. Optical microscopy, scanning electron microscopy, transmission electron microscopy, and electron dispersion x-ray spectroscopy are used to examine  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  quantum well heterostructure material that has hydrolyzed at cleaved edges, cracks and fissures, and at pinholes in cap layers. The hydrolysis is found to be significant for thicker ( $> 0.1\ \mu\text{m}$ )  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  layers of higher composition ( $x > 0.85$ ).



AN OVERVIEW OF EARLY STUDIES ON PERSISTENT PHOTOCONDUCTIVITY  
AND OTHER PROPERTIES OF DEEP LEVELS IN GaAsP:  
THE EFFECT OF DEEP LEVELS  
ON LIGHT EMITTING DEVICES

by

M. George Craford  
Hewlett Packard Company  
Optoelectronics Division  
San Jose, California 95131

G.E. Stillman, and N. Holonyak, Jr.  
Electrical Engineering Research Lab., and Materials Research Lab.  
University of Illinois at Urbana-Champaign  
Urbana, Illinois 61801

J.A. Rossi  
Monsanto Electronic Materials Company  
St. Peters, Missouri 63376

ABSTRACT

Laser studies carried out at the University of Illinois in 1966 showed that the shortest wavelength at which lasing could be achieved in GaAsP was dependent on the n-type dopant. In particular sulfur doping was found to restrict lasing to longer wavelengths. It was suggested that this could be due to the effect of energy levels associated with the higher conduction band minima. This led in 1967 to an investigation of the effect of Te and S donor levels on the properties of GaAsP near the direct - indirect crossover. Samples throughout the composition range were studied using Hall effect measurements from 55 to 400°K and resistivity measurements under hydrostatic pressure between 0 and 7 kbar at 300, 195, and 77°K. The data on Te-doped samples fit the standard energy band models, but S doping was found to exhibit dramatic persistent photoconductivity and other compositional effects similar to the "DX-center" effects later observed in AlGaAs and other materials.

This paper summarizes these results on GaAsP:S, and gives a brief overview of other early investigations in compound semiconductors where energy levels associated with higher lying minima were studied and where, in some cases, nonequilibrium effects were observed. A later study on GaAsP:S is also described which shows the effect of S-doping on LED performance. Finally, some of the implications that the existence of deep levels of this type have on light emitting device performance in other alloy systems is discussed.

HYDROGENATION OF Si- AND Be-DOPED InGaP

J. M. Dallesasse, I. Szafranek, J. N. Baillargeon, N. El-Zein,  
N. Holonyak, Jr., G. E. Stillman, and K. Y. Cheng

Electrical Engineering Research Laboratory,  
Center for Compound Semiconductor Microelectronics, and  
Materials Research Laboratory

University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

ABSTRACT

Data are presented on the hydrogenation of Be-doped (p-type) and Si-doped (n-type)  $\text{In}_{1-x}\text{Ga}_x\text{P}$  epitaxial layers grown lattice matched to GaAs ( $x \sim 0.5$ ). Low-temperature (1.7 K) photoluminescence, electrochemical carrier concentration profiling, and scanning electron microscopy are used to study the effects of hydrogenation on carrier recombination, carrier concentration, and surface morphology. Hydrogenation is found to passivate Si donors and Be acceptors and to improve photoluminescence efficiency, but causes mild surface damage. The carrier concentration following hydrogenation is found to be lowest in acceptor-doped material.

HYDROGENATION-DEFINED STRIPE-GEOMETRY  $\text{In}_{0.5}(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{P}$   
QUANTUM WELL LASERS

J. M. Dallesasse, N. El-Zein, and N. Holonyak, Jr.

Electrical Engineering Research Laboratory,  
Center for Compound Semiconductor Microelectronics, and  
Materials Research Laboratory

University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

R. M. Fletcher, C. P. Kuo, T. D. Osentowski, and M. G. Craford  
Hewlett Packard Optoelectronics Division, San Jose, California 95131

ABSTRACT

Data are presented on the continuous-wave (cw), room-temperature (300 K) operation of stripe-geometry  $\text{In}_{0.5}(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{P}$  quantum well heterostructure lasers defined via hydrogenation. Passivation of the Zn acceptors in the cap and upper confining layer provides gain-guiding, and elimination of the current-blocking oxide reduces the thermal impedance. The resultant device is capable of better performance than conventional oxide-stripe diodes fabricated on the same material.

LAYER DISORDERING IN HEAVILY CARBON-DOPED  
AlGaAs/GaAs SUPERLATTICES

I. Szafranek, M. Szafranek, B.T. Cunningham,  
N. Holonyak, Jr. and G.E. Stillman

Center for Compound Semiconductor Microelectronics, Materials Research Laboratory and  
Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, IL 61801

ABSTRACT

Interdiffusion of Al and Ga in heavily C-doped  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}/\text{GaAs}$  superlattice (SL) structures has been investigated for a variety of ambient and surface encapsulation conditions. High-resolution photoluminescence (PL) at  $T=1.7$  K was employed to evaluate the extent of layer intermixing after 24 hour anneals at  $825^\circ\text{C}$ . From the shifts to higher energies of the PL peaks due to  $n=1$  electron-to-heavy hole transitions in the quantum wells of the annealed SLs relative to the position of this peak in the as-grown crystal, approximate Al-Ga interdiffusion coefficients,  $D$ , have been determined for different annealing conditions. For all encapsulants studied the interdiffusion in C-doped crystals is accelerated under As-rich, and impeded under a very As-deficient ambient atmosphere. This result disagrees with previously observed trends in Group II-doped p-type structures, which have led to the charge point-defect model of Al-Ga interdiffusion. The  $\text{Si}_3\text{N}_4$  cap has provided the most effective surface sealing against ambient-stimulated layer interdiffusion, and yielded  $D = 1.7 - 4.0 \times 10^{-19} \text{ cm}^2/\text{sec}$ . The most extensive layer intermixing has been observed for uncapped SL annealed under As-rich ambient ( $D = 3.3 \times 10^{-18} \text{ cm}^2/\text{sec}$ ). These values are up to  $\sim 40$  times greater than those previously reported for nominally undoped  $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$  SLs, implying that the  $\text{C}_{\text{As}}$  doping slightly enhances host-atom self-diffusion on the Group III sublattice. Pronounced

changes in the PL spectra have been observed for some annealed samples stored at room temperature. These long-term fluctuations in optical properties, reported here for the first time, may be indicative of degraded thermal stability of the annealed SL crystals due to high-temperature-induced lattice defects.

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