Midwave Infrared (2-6μm) Emitter-Based Chemical Sensor Systems

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MIDWAVE INFRARED (2-6μm) EMITTER-BASED CHEMICAL SENSOR SYSTEMS

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Abstract

Novel mid-infrared (≈4μm wavelength) lasers and light-emitting diodes (LEDs) were constructed from InAsSb-based heterostructures. These devices were grown by metal-organic chemical vapor deposition (MOCVD). For injection and optically pumped lasers, operation above 200K was demonstrated. The first type I, MOCVD-grown "cascaded" mid-infrared laser also was demonstrated. An InAsSb superlattice LED-based carbon dioxide detection system is described.
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1. INTRODUCTION

Long wavelength (2-6 μm) diode emitters are desirable for many applications including monitoring of chemical species in the environment and manufacturing, long wavelength fiber-optic communications, lidar, and IR detector counter-measures. No practical diode lasers are available for any of these applications because the band structure of bulk III-V, II-VI, and IV-VI semiconductor alloys results in large Auger recombination rates at these wavelengths. Experimental and theoretical work at Sandia has resulted in new understanding of the electronic properties of narrow bandgap III-V heterostructures, and we have found methods of reducing the Auger rates in certain InAsSb superlattices and quantum wells. These devices enable us to begin chemical sensing demonstrations of important species such as CO-CO₂ and numerous other compounds. This project will involve developing chemical sensing systems and determining the sensitivity and limitations of these systems. Concurrently, we will improve upon infrared emitters used in these systems.

2. THE GROWTH AND CHARACTERIZATION OF InAsSb BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION (MOCVD)

We have investigated the use of several different types of active regions for the infrared emitters. Our best results to date were have been achieved with InAsSb/InAsP SLSs. We optimized the growth of these structures by first investigating the growth of InAsSb/InAs and InAsP/InAs multiple quantum well (MQW) structures. We used a growth rate of 0.28 nm/s and purge times of 15 to 20 seconds with arsenic flowing during the purge between InAs and the ternary layer growth to allow for source flow changes
during the growth of the MQWs. A low V/III ratio is necessary for the growth of high quality InAsSb due to the low vapor pressure of Sb; excess Sb tends to cause surface morphology defects. For InAsP, the V/III ratio is dominated by the excess phosphine flow and was approximately constant at 70. The high V/III ratio and excess phosphine flow are necessary because of the high decomposition temperature of phosphine. In both cases, InAsSb/InAs and InAsP/InAs, the composition dependence was reproducible and approximately linear over the composition range that was examined. The composition range for InAs$_{1-x}$Sb$_x$ was 0.06<$x$<0.25 and for InAs$_{1-x}$P$_x$, 0.1<$x$<0.6.

The growth of the InAsSb/InAsP ternary strained-layer superlattices (SLSs) used similar conditions as those for the MQW growths. The growth conditions for a given composition of the SLS were easily predicted from the compositions of the MQW’s. However, very rough surface morphologies and poor x-ray diffraction patterns and photoluminescence characteristics were found for the SLSs for the 15-20 second purge times that were used between the layers for the MQWs. The purge times for the InAsSb/InAsP SLSs were optimized using both x-ray diffraction patterns.

We have used both InPSb and AlAsSb as confinement materials for our infrared emitters. AlSb and AlAs$_x$Sb$_{1-x}$ are of interest for their potential application as optical and electronic confinement layers in a variety of optoelectronic devices such as infrared detectors, resonant tunneling diodes, and laser diodes. The refractive index difference between AlAsSb and InAs is larger than that between InPSb and InAs and, therefore, better optical confinement should be achieved using AlAsSb for confinement rather than InPSb. In our work, we applied an analogous approach to that used for reducing the carbon concentration in AlGaAs where trimethylamine alane (TMAA) and
triethylgallium (TEGa) were used to prepare high purity AlGaAs. We have used TMAA or ethyldimethylamine alane (EDMAA) and triethylantimony (TESb) to prepare AlAsSb by MOCVD]. Our most recent and best mid-wave infrared emitter results have used AlAsSb]. During growth of the emitter structures in a conventional horizontal reactor we encountered Al memory effects when trying to grow active regions for emitters on top of the AlAsSb. In order to prepare the emitters using AlAsSb layers in the horizontal reactor, we developed a regrowth technique]. We have since avoided this difficulty by using a high speed rotating disk reactor (RDR) to prepare the infrared emitters using AlAsSb without a regrowth step. We have also successfully used this type of reactor to prepare cascaded structures as discussed in more detail below.

The best growth conditions for AlAs\textsubscript{x}Sb\textsubscript{1-x} in our RDR occurred at 500 °C and 70 torr at a growth rate of 3.2 Å/s using a V/III ratio of 5.3. The V/III ratio was calculated using a vapor pressure of 0.75 torr for ethyldimethylamine alane (EDMAA) at 19.8 °C and an triethylantimony [TESb]/(tertiarybutyl arsine[TBAs]+[TESb]) ratio of 0.83. The growth rate was found to be dependent on the EDMAA flow and independent of the group V flows. The best surface morphologies with the lowest number of defects were obtained by using a buffer layer grown before the AlAs\textsubscript{x}Sb\textsubscript{1-x} layer. The defects consisted primarily of square pyramidal hillocks 10 to 20 μm on a side. Lattice matched AlAs\textsubscript{x}Sb\textsubscript{1-x} films of high crystalline quality, as evidenced by x-ray diffraction where full widths at half of the maximum intensity (FWHM) of 27 to 50 arc seconds were obtained. Typical InAs substrate peaks measured 10-20 arc seconds for the FWHM. The x-ray peak width of 50 arc seconds could be due to some variation in composition with growth time as discussed below or to phase separation. We were also able to reproducibly obtain lattice
matching of AlAs$_x$Sb$_{1-x}$ to InAs to within less than 0.00015 using the optimized growth conditions. Hall measurements of AlAsSb films 1 µm thick with 200Å GaAsSb cap layers grown on GaAs substrates indicated background hole concentrations between 0.5 to 1 x10$^{17}$ cm$^{-3}$. The residual hole concentration of GaAsSb films on GaAs ranged between 4 to 7x10$^{16}$ cm$^{-3}$. The use of other than the above stated growth conditions led to several significant problems during the growth of AlAs$_x$Sb$_{1-x}$ layers lattice matched to InAs. These included composition control and reproducibility. For instance, growth at higher V/III ratios resulted in a large drift in composition from run to run and broad x-ray diffraction peaks. Composition variations have also been observed due to excess cooling of the chamber walls due to an Sb memory effect on the inlet to the reactor.

We have successfully doped the AlAs$_x$Sb$_{1-x}$ layers p-type using DEZn. We achieved p-type levels of 1 x 10$^{16}$ to 6 x 10$^{17}$ cm$^{-3}$. The mobilities for the AlAs$_x$Sb$_{1-x}$ layers ranged from 200 to 50 cm$^2$/Vs with no clear trend that could be associated with the carrier concentration. The Zn doping levels were determined from Van der Pauw/Hall measurements and confirmed by secondary ion mass spectroscopy (SIMS) on thick calibration samples. SIMS measurements on the Zn doped samples indicated a similar level of Zn compared to the p-type carriers indicating complete activation of the Zn. Two orders of magnitude higher DEZn partial pressures were required to obtain equivalent dopant levels in AlAs$_{0.16}$Sb$_{0.84}$ compared to GaAs$_{0.09}$Sb$_{0.91}$. This lower incorporation rate for Zn in AlAsSb indicates a possible depletion reaction between DEZn and EDMAA.
3. INFRARED DEVICE RESULTS

3.1 As-Rich, InAsSb Superlattices and Mid-Wave Infrared Lasers and Light Emitting Diodes

As-rich InAsSb SLSs were developed as novel active regions for mid-wave infrared (MWIR) lasers. The performance of MWIR lasers has been limited by Auger recombination, which dominates radiative recombination in narrow bandgap semiconductors. Potentially, Auger recombination can be suppressed in “band-structure engineered” InAsSb heterostructures. Limited by critical layer thickness considerations, high quality InAsSb SLSs and quantum-wells span the 3-6 μm, MWIR wavelength range. As-rich, InAsSb SLSs can be grown strain-balanced and lattice-matched to InAs or GaSb substrates, thus eliminating the need for strain-relief buffers. Since background doping levels are not usually a factor in laser performance, InAsSb lasers could be grown using either MOCVD or MBE. Unless noted otherwise, all of the devices described in this section were grown by MOCVD.

In As-rich, InAsSb SLS laser active regions, holes are confined to compressively strained layers, producing a low in-plane, effective mass \( \ell^{3/2} \) hole ground state. In compressively strained InAsSb SLSs, it is necessary to maximize the light-heavy \( \ell^{3/2} \) hole splitting to suppress Auger recombination.

Towards this goal, MBE-grown InAsSb/InAlAs and InAsSb/InAlAsSb SLS lasers were investigated with encouraging results [1,2]. In our work, we reported the properties of the first InAsSb/InAsP SLS materials and devices [3]. The InAsSb/InAsP SLS is an “MOCVD variant” of the most promising type I, strained InAsSb heterostructures for
Auger suppression, and a miscibility gap, reported for InAlAsSb quaternaries [4], has not been encountered for InAsP. Incorporating InAsP as a barrier layer in the SLS active region introduces a larger valence band offset when compared to that between InAs or InGaAs and InAsSb.

The band alignments and quantum confinement states for a representative InAsSb/InAsP SLS active region are shown in Figure 1 [5]. The energy levels for this InAs$_{0.88}$Sb$_{0.12}$/$\text{InAs}_{0.76}$P$_{0.24}$ (80 Å/80 Å) SLS were determined using a transfer matrix, 8x8 $\mathbf{k}\cdot\mathbf{p}$ calculation. Based on previous measurements of our ordered and phase separated, MOCVD-grown, InAsSb alloys, the estimated bandgap of the unstrained InAs$_{0.88}$Sb$_{0.12}$ alloy was 259 meV [6,7]. SLS valence band offsets vary linearly with composition from unstrained InAs/InSb and InAs/InP valence band offset values, 0.39 eV [8] and -0.56 eV, respectively [9]. When used as the active region, the SLS in Figure 1 will emit at 349 meV (3.6 μm) at low temperature. We estimate that the SLS has a light-heavy hole splitting of 69 meV. Limited by critical layer thickness, longer wavelength InAsSb/InAsP SLSs with higher Sb and P content will display even larger light-heavy hole splittings.

To avoid loss mechanisms associated with electrical injection and to observe lasing with minimum heating, our initial InAsSb/InAsP SLS lasers were characterized using low duty-cycle optical pumping [10]. An optically pumped laser was grown on an InAs substrate with a 2.5 μm thick AlAs$_{0.16}$Sb$_{0.84}$ lower cladding. On top of the cladding, the active region was a 1.0 μm thick, InAs$_{0.89}$Sb$_{0.11}$/InAs$_{0.77}$P$_{0.23}$ (83 Å/87 Å) SLS. The SLS laser was pumped with a Q-switched Nd:YAG (1.06 μm, 20 Hz, 10 ns pulse, focused to a 200 μm wide line), and emission was detected with an FTIR operated in a
Figure 1. - Band alignments and quantum confinement state energies (drawn to scale) for an InAs$_{0.88}$Sb$_{0.12}$ / InAs$_{0.77}$P$_{0.23}$ (83 Å / 87 Å) SLS.

Figure 2 - Lasing and PL spectra for a laser with an InAs$_{0.89}$Sb$_{0.11}$ / InAs$_{0.77}$P$_{0.23}$ (83 Å / 87 Å) SLS active region.
Figure 3 - (a) Pulsed laser emission intensity versus optical pump power for various temperatures for an InAs$_{0.89}$Sb$_{0.11}$ /InAs$_{0.77}$P$_{0.23}$ (83 Å / 87 Å) SLS active region.
(b) Threshold optical pump power versus temperature.

Figure 4 - A band diagram of our multi-stage, "cascaded" active region, under forward bias. heterojunction.
step-scan mode. Due to the low rep-rate of the pump, approximately a 4 hour scan was required to obtain an interferogram with resolution \( \geq 2 \text{ cm}^{-1} \).

Laser emission was observed from cleaved bars, 1000\,\mu m wide, with uncoated facets [5]. A lasing threshold and spectrally narrowed, laser emission was seen from 80 K through 240 K, the maximum temperature where lasing occurred. (See Figure 2 and 3(a)) As shown in Figure 2, the PL line-width was \( \approx 25 \text{ meV} \) at 80K, but above threshold, the laser emission, narrowed to 3-5 meV, depending on the sample. The laser emission line-width was limited by inhomogenieties in the material and the presence of multiple, unresolved longitudinal modes. The wavelength of our laser shifted from 3.57\,\mu m to 3.85\,\mu m due to the decrease in bandgap over the 80-240K temperature range. At 80 K, peak powers >500 mW/facet could be obtained. The temperature dependence of the SLS laser threshold is described by a characteristic temperature, \( T_0 = 33 \text{ K} \), over the entire range (See Figure 3(b)) [5].

3.2 Cascaded Mid-infrared Lasers with InAsSb Quantum Wells

Having demonstrated optically pumped lasers with InAsSb/InAsP SLS active regions, we demonstrated several InAsSb/InAsP SLS injection devices, culminating with "cascaded" InAsSb/InAsP SLS lasers [10]. A band diagram of our multi-stage, "cascaded" active region, under forward bias, is shown in Figure 4a. Electron-hole recombination occurred in compressively strained InAsSb quantum wells separated by tensile strained InAsP barriers. The type I, InAsSb/InAsP quantum wells had a large light-heavy hole splitting required for suppression of Auger recombination [5]. Electron-hole pairs for each stage were generated at a semi-metal, GaAsSb (p)/ InAs (n). An
AlAsSb layer prevented electrons from escaping; nominal hole confinement was provided by the InAsSb quantum well valence band offset in this initial device. Ideally, in the absence of non-radiative loses, electron-hole generation replenishes the carriers which recombine in each stage, and for each carrier injected from the external circuit, the multi-stage active region can emit several photons resulting in an overall quantum efficiency greater than unity. In practice, charge can build-up in the active region, shift the Fermi-level, and turn-off electron generation at the semi-metal.

Unlike previous cascaded lasers, our device was grown by MOCVD [10]. These devices are among the most complex structures ever grown by MOCVD. The gain region of our laser was composed of 10 stages. Each stage consisted of a GaAs$_{0.09}$Sb$_{0.91}$ (p, 300 Å)/InAs (n, 500 Å) semi-metal, 5 InAs$_{0.85}$Sb$_{0.15}$ (n, 94 Å) quantum wells separated by 6 InAs$_{0.87}$P$_{0.13}$ (n, 95 Å) barriers, an AlAs$_{0.16}$Sb$_{0.84}$ (p, 50 Å) electron block, a compositionally graded, Zn-doped AlGaAsSb (p = 5 x 10$^{17}$ cm$^{-3}$, 300 Å) layer and a final 50 Å, Zn-doped GaAs$_{0.09}$Sb$_{0.91}$ layer. The total thickness of the gain region is 2.2 μm. The excellent crystalline quality of the laser structure was demonstrated in the x-ray diffraction spectrum where groups of satellite peaks corresponding to the gain-stage period of 2100 Å and the InAsSb/InAsP period of 190 Å are observed. Optical confinement was provided by 2 μm thick, Zn-doped AlAs$_{0.16}$Sb$_{0.84}$ (p = 1 x 10$^{17}$ cm$^{-3}$) claddings on both sides of the active region. A top 1500 Å Zn-doped GaAs$_{0.09}$Sb$_{0.91}$ layer (p=2 x 10$^{18}$ cm$^{-3}$) was used as a contact and protective layer. The structure is lattice matched to the InAs substrate.

The narrow LED and photoluminescence emission peaks of the 10-stage laser wafer indicated good stage-to-stage uniformity of the InAsSb/InAsP multiple quantum
wells. Only InAsSb/InAsP emission was observed in the LED spectrum. Emission from the InAs layer would be strong indication of inadequate carrier confinement by the InAsSb quantum wells. The LED emission wavelength shifted from 3.7 \( \mu \text{m} \) (80 K) to 4.3 \( \mu \text{m} \) (300 K) due to the temperature dependence of the InAsSb/InAsP bandgap. Operated at 50% duty cycle, average LED output powers were 2.4 mW at 80 K and 100 \( \mu \text{W} \) at 300 K when driven with 200 mA average current. Our LED power was much greater than that of liquid-phase epitaxy-grown InAsSb alloy LEDs (\( \approx 10 \mu \text{W} @ 300 \text{K} \)), obtained commercially. We speculate that the rapid decrease in LED power with temperature was due to thermal emission of holes from the InAsSb/InAsP quantum wells.

Lasing was observed from gain-guided stripe lasers. The facets were uncoated, and stripes were indium soldered to the heat sink with the epitaxial side up. Under pulsed
operation with 100 ns pulses at 1 kHz ($10^{-4}$ duty-cycle), stimulated emission was observed from 80-180 K. Laser emission spectra at 80 K and 150 K are shown in Figure 5(a). Emission occurred at 3.8-3.9 μm. For 500 μm long stripes with 80 μm wide metallizations, several longitudinal modes are observed with a mode spacing of 2.7 cm$^{-1}$, corresponding to a mode index of 3.7. The longest laser pulses were 1 μs. These initial devices were easily damaged by increased heating associated with higher temperature operation or longer duty cycles.

Threshold current densities for these 10-stage devices were $\geq 1$ kA/cm$^2$. Although these values are over-estimates due to current spreading in our gain-guided
structures, reduction of threshold current density has not yet been demonstrated in type I (InAsSb) or type II (InAs/InGaSb) cascaded interband lasers [12]. Lower threshold current densities (0.1 kA/cm²) have been demonstrated in single-stage, type I mid-infrared lasers at 80 K [1]. The temperature dependence of the threshold current is shown in Figure 5(b) for an 80x250 µm, 10-stage laser. Similar to optically pumped InAsSb/InAsP lasers, the characteristic temperature is roughly 34 K [10,11].

The laser output was collected and focused directly onto an InSb detector to obtain power-current data shown in Figure 6(a) [10]. At 80 K, peak power values >100 mW were obtained. The maximum slope-efficiency was 150 mW/A, corresponding to a differential external quantum efficiency of 48% (4.8% per stage). This result approaches the value obtained for a second generation, 23-stage type II cascaded laser (3.9 µm) with a differential quantum efficiency of 131% (5.7 % per stage) [12]. These slope-efficiencies are under-estimates due to current spreading in the gain-guided structures.

To further illustrate the effects of multi-staging, we constructed a laser with a single-stage InAsSb/InAsP multiple quantum well active region. At 80 K, the slope efficiency of an 80x1000 µm single-stage device was 2 mW/A, whereas the slope efficiency of the 10-stage, 80x1000 µm laser was 34 mW/A.

Multi-stage laser slope-efficiency (or differential-efficiency) was strongly dependent on cavity length [10]. Power-current curves for 10-stage laser stripes with lengths of 250-1000 µm are shown in Figure 6(a). These results are plotted as (differential-efficiency)^{-1} versus cavity length in Figure 6(b). Scatter in the data prevents accurate determination of internal efficiency and loss coefficient, but the best fits are obtained for internal efficiency values in the range 1-10, strongly suggesting an internal
quantum efficiency > 1. Depending on this internal efficiency value, we obtain a loss coefficient $\geq 100 \text{ cm}^{-1}$ for our devices. Large losses may be caused by intersubband absorption of the InAsSb/InAsP quantum wells or free carrier absorption in semimetal layers or heavily doped cladding and heterobarrier layers. Comparison of absorption spectra for single-stage and 10-stage laser wafers reveals absorption of the correct magnitude associated with the 10-stage gain region, suggesting that the loss originates from the semimetal design or doping in the active region. A lower sheet carrier density can be achieved with quantum confinement of the semimetal, like that used in type II cascade laser designs [12]. We doubt that absorption in the InAsSb quantum wells is causing the loss because such high loss has not been observed in other type I, Sb-based lasers. Reduction of loss will be a major hurdle in the advancement of Sb-based, injection lasers, especially cascaded devices.

4. LED-Based Gas Sensing

LEDs like those in section 3.1 were used to demonstrate a high sensitivity, broadband gas sensor system. The LEDs were operated at 300 K, and the system used a single, TE cooled PbSe infrared detector. Care was taken to compensate for thermal drift of the detector and LED. CO$_2$ sensing at 4.2 $\mu$m was demonstrated using a gas test bed system to accurately control the gas mixture and flow to an optical transmission cell. During the experiment, dilute CO$_2$ in N$_2$ mixtures and N$_2$ purges were alternated at 30 minute intervals. As shown in Figure 7, CO$_2$ detection was demonstrated for concentrations in the 100-24 ppm range. Based on system signal/noise considerations,
we estimate that this prototype gas sensing system can detect CO₂ concentrations ≥ 10 ppm.

**Figure 7**- Gas sensor system response to different CO₂ concentrations followed by N₂ purges.

5. SUMMARY AND FUTURE DIRECTIONS

We have used As-rich, InAsSb SLSs as active regions for MOCVD-grown, mid-infrared lasers and LEDs (3 to 6 µm). These devices were among the first to utilize strain, or symmetry-breaking, to lower Auger recombination and improve III-V, mid-infrared emitter performance. We have reported the first cascaded lasers and LEDs with type I InAsSb quantum well active regions. These are the first cascaded devices grown
by MOCVD. We are optimistic that advances in material quality and device design will improve carrier confinement and reduce loss, leading to higher efficiencies and higher temperature operation of cascaded InAsSb lasers. With nominal improvements in materials and processing and the further development of multi-stage active regions, MOCVD-grown InAsSb devices should be able to satisfy the system requirements for use in chemical sensor and infrared countermeasure technologies in the near future.
REFERENCES

Appendix

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