Development of InAsSb-based light emitting diodes for chemical sensing systems

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ABSTRACT

Mid-infrared (3-6μm) LED's are being developed for use in chemical sensor systems. As-rich, InAsSb heterostructures are particularly suited for optical emitters in the mid-infrared region. We are investigating both InAsSb-InAs multiple quantum well (MQW) and InAsSb-InAsP strained layer superlattice (SLS) structures for use as the active region for light emitting diodes (LED's). The addition of phosphorus to the InAs barriers increases the light and heavy hole splitting and hence reduces non-radiative Auger recombination and provides for better electron and hole confinement in the InAsSb quantum well. Low temperature (<20K) photoluminescence (PL) emission from MQW structures is observed between 3.2 to 6.0μm for InAsSb wells between 70 to 100Å and antimony mole fractions between 0.04 to 0.18. Room temperature PL has been observed to 6.4 μm in MQW structures. The additional confinement by InAsP barriers results in low temperature PL being observed over a narrower range (3.2 to 5.0μm) for the similar well thicknesses with antimony mole fractions between 0.10 to 0.24. Room temperature photoluminescence was observed to 5.8μm in SLS structures.

The addition of a p-AlAsSb layer between the n-type active region (MQW or SLS) and a p-GaAsSb contact layer improves electron confinement of the active region and increases output power by a factor of 4. Simple LED emitters have been fabricated which exhibit an average power at room temperature of >100μW at 4.0μm for SLS active regions. These LED's have been used to detect CO_2 concentrations down to 24ppm in a first generation, non-cryogenic sensor system. We will report on the development of novel LED device designs that are expected to lead to further improvements in output power.

Keywords: InAsSb, Light Emitting Diodes, Mid-Infrared LED, MOCVD

1. INTRODUCTION

Many molecules have strong vibrational absorption bands over the mid-infrared (3-6μm) region. Molecules with C-H bonds such as Benzene and Methane have strong absorption bands around 3-3.4μm. Gases like CO_2 (4.2μm), CO (4.7μm), NO_2 (4.5μm) and NO (5.3μm) have absorption bands between 4 and 6μm. Light emitting diodes and laser diodes that employ As-rich, InAsSb heterostructures are particularly suited for optical emitters in the mid-infrared region. However unlike laser diodes in this material system, LED's operate at room temperature and are easier to fabricate.

In this paper we report on the performance of several LED device structures employing two InAsSb based active regions. All structures were grown by MOCVD. The active regions consisted of either a InAs-InAsSb multi-quantum well (MQW) or a InAsP-InAsSb strained layer superlattice (SLS). We present the growth conditions and interface transitions that lead to improved photoluminescence from these active regions.

DISCLAIMER

2. EXPERIMENT

This work was carried out in a previously described vertical Rotating Disk Reactor (RDR).[1] This reactor geometry avoids the memory effects we experienced in a reactor with a horizontal chamber.[2] Ethyldimethylamine alane (EDMAA), triethylgallium (TEG), triethylantimony (TESb), trimethylindium (TMIn) and phosphine were the sources for Al, Ga, Sb, In and P respectively. Tertiarybutylarsine (TBA) and 100% arsine were used as a source of arsenic. Undoped, n-type InAs (100) substrates were used for all growths.

LED emitters were fabricated using one of two active regions. The first consisted of a 10 period multi-quantum well (MQW) structure of 70-100Å InAsSb quantum wells with 350-500Å InAs barriers. The other consisted of a 5 to 40 period strained layer superlattice (SLS) with the 40-110Å InAsSb wells but with 60-100 Å InAsP barriers. The antimony mole fraction ranged from 0.04 to 0.18 in the MQW structures and 0.10 to 0.24 in the SLS structures. These structures were all grown at 500°C and 70torr. The addition of phosphorous to the InAs barriers provides better electron and hole confinement in the quantum well and allows the superlattice structure to be strain balanced to InAs substrates.

Five crystal x-ray diffraction (FCXRD) was used to determine the alloy composition and superlattice period. Photoluminescence at 16K and 300K was used to characterize the optical quality of the active region. LED devices were fabricated from samples cleaved to 4-9mm^2 with 0.74mm diameter contacts on top and a metalized backside. All metalizations consisted of 50Å of Ti followed by 2000Å of Au. Electroluminescence (EL) measurements were made using modulation techniques at 1KHz with a 50% duty cycle and an InSb detector

3. GROWTH OF InAs-InAsSb MQW ACTIVE REGIONS

The details of the growth of the InAs-InAsSb multiple quantum well (MQW) structures with AsH_3 on InAs have been previously published.[2,3] Typical x-ray diffraction patterns of MQW structures had sharp satellite peaks out to n=8 indicating good crystalline structure. The MQW structures were grown at 500 °C, 70torr, at a growth rate of 3.1Å/sec. The V/III ratio varied between 3 and 15. The antimony mole fraction of the $InAs_{1-x}Sb_x$ quantum wells could be varied between x = 0.04 and 0.12 by changing the Sb/V ratio between 0.07 and 0.26. The composition changes can be explained by the use of a thermodynamic model as previously discussed.[3] Low temperature (16K) photoluminescence is observed between 3.5 to 4.5μm for these structures (Figure 1.). Wavelengths to 6.0μm have been observed by increasing the antimony composition of the quantum wells. The background doping of the InAs-InAsSb active region is n-type, 10^{15}-10^{16} /cm^3. These results are similar to that observed from MQW's grown with a horizontal chamber reactor.

The RDR system used in this study had one AsH_3 line. This necessitated a 15 second growth interruption between each layer in the MQW structure to allow the mass flow controller to stabilize. The presence or absence of AsH_3 during this interruption had a significant impact on the well composition, PL wavelength and intensity. Two MQW structures were grown under identical conditions except for the presence or absence of AsH_3 during the growth interruption. The sample with AsH_3 present showed a lower antimony composition (11%) than the sample with only H_2 present (13%). The sample with the lower composition had a shorter wavelength PL (16K) emission (4.20 μm vs. 4.46μm) as would be expected but also had 3 times the intensity. Consequently an AsH_3 over-pressure was maintained during growth interrupts in MQW structures grown with AsH_3

To avoid a growth interruption, InAsSb quantum wells were grown using TBA. MQW structures were grown using a V/III ratio between 1.9 to 5.9 and Sb/V ratio between 0.18 and 0.48. The well composition varied between 0.04 to 0.14 for the conditions investigated. The low temperature PL ranged between 3.0 to 4.5μm for these samples. (Figure 1.) The best PL intensities for InAsSb quantum wells grown with TBA were obtained when there was no growth interruption between layers. For the same Sb/V ratio, InAsSb layers grown with TBA had lower antimony compositions than these grown with AsH_3. This is consistent with the better decomposition of TBA at 500°C which results in lower antimony incorporation. There was no significant difference in PL intensity from MQW structures grown with TBA versus AsH_3. (Figure 2.)

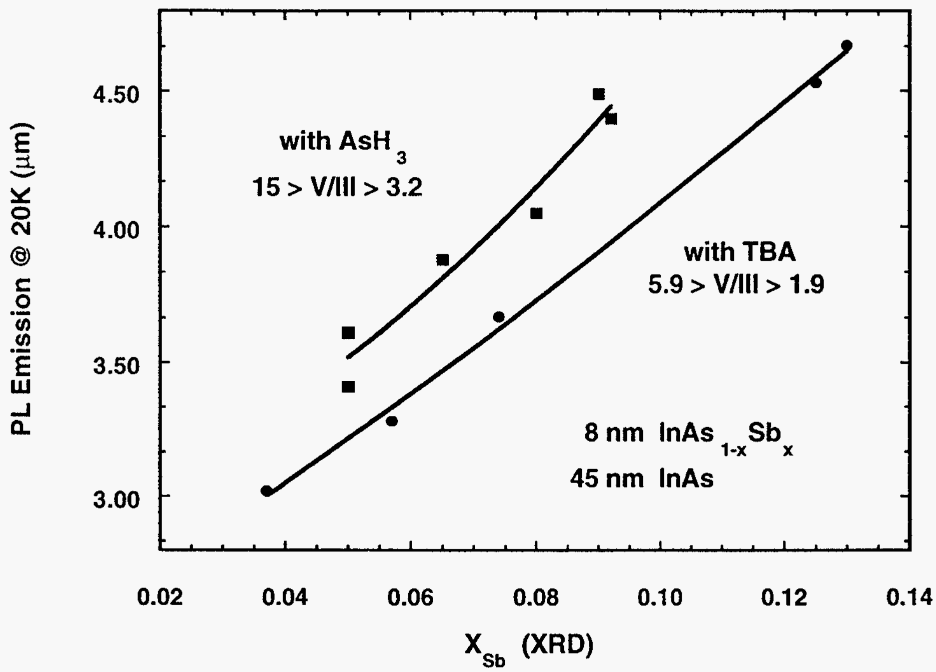

Figure 1. Low temperature (16K) photoluminescence from 10 period a 80Å $InAs_{1-x}$ Sb_x / 450Å InAs MQW's grown with (•) TBA, or with (■) AsH_3. InAs was grown using AsH_3 in all structures.

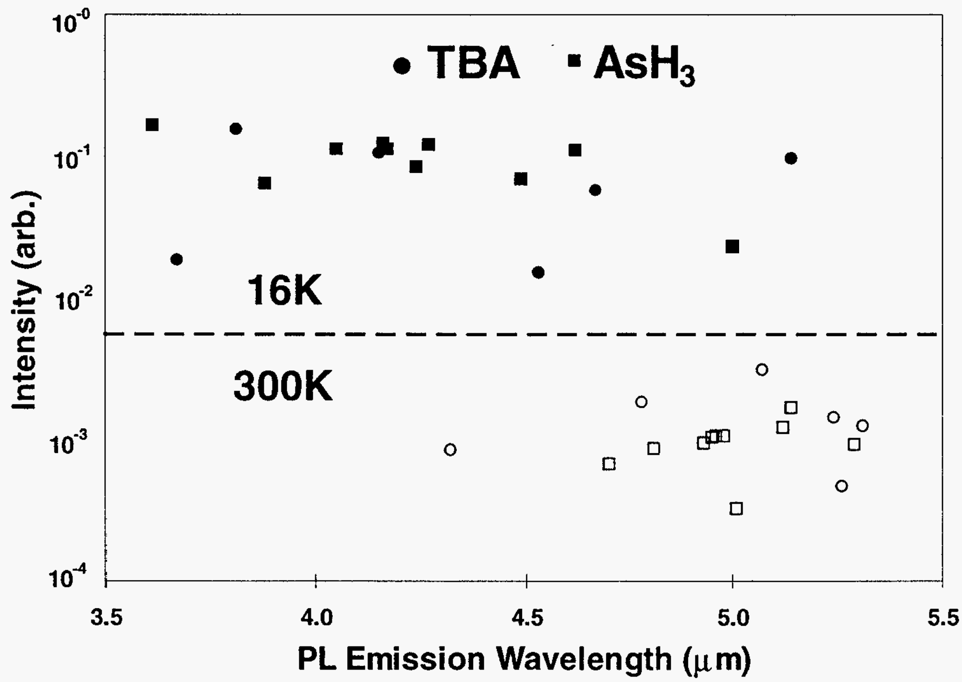

Figure 2. Photoluminescence intensity at 16K and 300K versus PL emission wavelength from $InAs_{1-x}$ Sb_x -InAs MQW structures grown with AsH_3 or TBA.

4. GROWTH OF InAsP-InAsSb SLS ACTIVE REGIONS

InAsP layers were grown using TBA and PH_3 at a V/III ratio of 22. The As/V ratio was changed to control the composition of the alloy and in some samples, to strain balance the SLS to InAs. Typical phosphorous mole fractions ranged between 0.25 to 0.35. PL emission from SLS structures were blue shifted relative to similar MQW structures due to the added confinement provided by the InAsP barriers. (Figures 2. and 3.) PL emission from 20 period SLS structures with fixed InAsP barrier and quantum well thickness was observed between 3.5 to 5μm at 16K and 4 to 5.8μm at 300K. PL emission could be adjusted from 3.2 to 3.8μm at 16K by changing the well thickness from 45Å to 110Å for structures with 78Å $InAs_{0.75}P_{0.25}$ barriers and $InAs_{0.89}Sb_{0.11}$ wells. The best PL intensity was obtained when a 1 second growth interrupt with AsH_3 was used between each layer. The AsH_3 flow used during the interruption was the same used to grown the InAsSb quantum well.

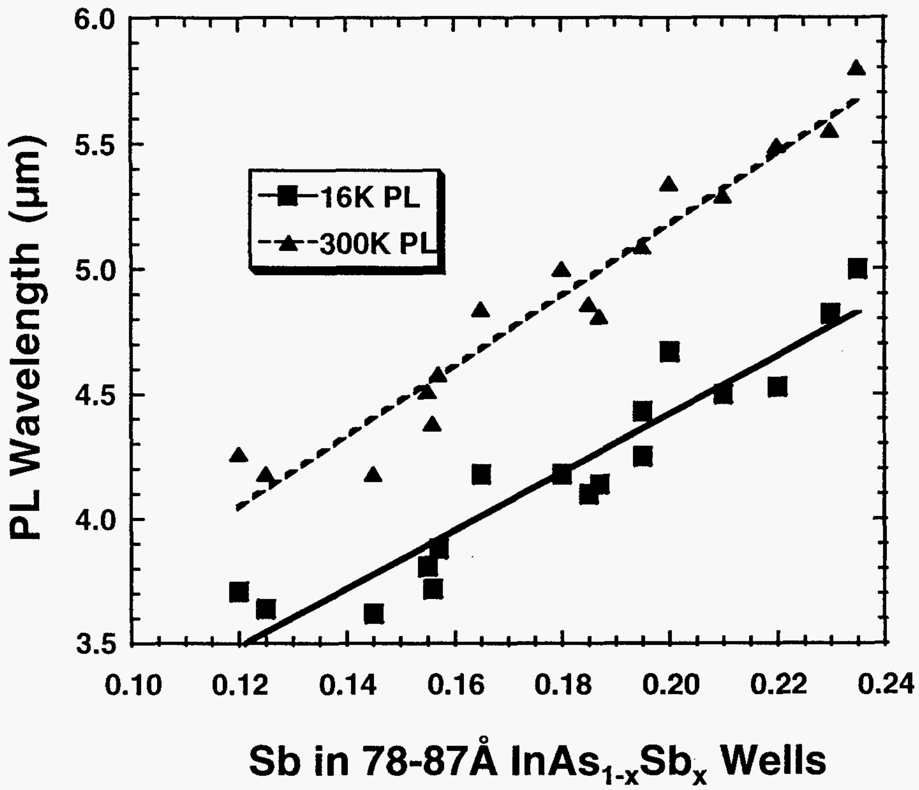

Figure 3. PL intensity at 300K was obtained from SLS structures between 4.1 to 5.8μm..

5. LED DEVICE STRUCTURES AND PERFROMANCE

We investigated three basic LED structures which are shown in Figure 4. The first is a p-n junction formed by doping the last several periods of the MQW or SLS active region with diethylzinc (DEZn). Electron confinement can be improved by adding an AlAsSb heterobarrier following the active region. This structure is capped with a GaAsSb layer for contacting and to prevent the AlAsSb from oxidizing. The AlAsSb next to the active region is undoped to avoid possible diffusion of zinc into the active region. An AlGaAsSb quaternary grade was used to improve hole transport between the AlAsSb heterobarrier and GaAsSb contact layer.

If an n-type InAs layer follows the p-GaAsSb cap layer a broken gap, type II band alignment is formed at this interface. That is, the valance band of GaAsSb is higher in energy than the condition band of InAs. This heterojunction acts as a semi-metal and can be a source or sink for electron-hole pairs. When a positive bias is applied to InAs, electrons are generated at the GaAsSb-InAs interface and move into the InAs layer. Charge is conserved by an equal number of holes being generated and moving into the GaAsSb layer. The use of the semi-metal interface or "injector" enables one to consider "cascaded" laser and LED designs that would not be feasible with conventional, p-n junction devices.[2] We have used this scheme to produce LED's and diode lasers with up to 10 stages.[4]

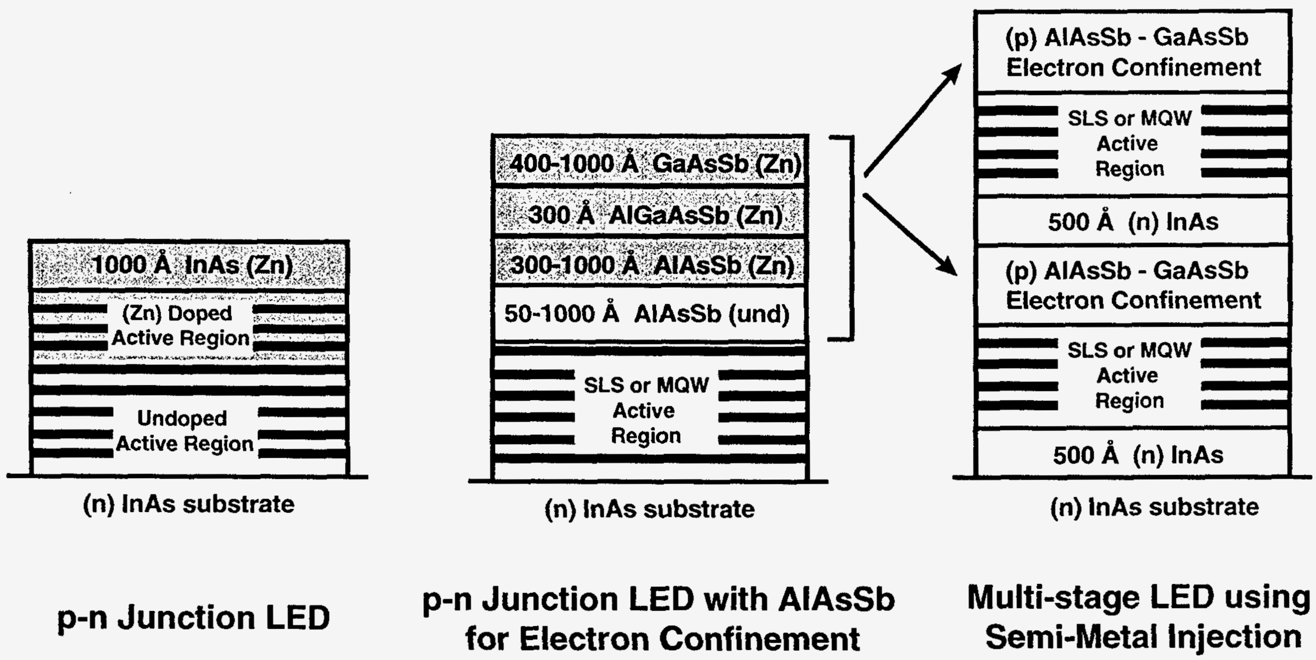

Figure 4. LED device structures investigated. AlAsSb provides a heterobarrier which confines electrons to the active region. A p-GaAsSb / n-InAs interface is used as an electron and hole source between active regions in the multistage device. Typical devices had 10 stages with each stage having 1 to 5 periods of MQW or SLS as the active region.

Figure 5 shows the LED emission at 300K of typical devices using either a 10 period MQW or a 5-10 period SLS active region. The devices shown all had AlAsSb heterobarriers and GaAsSb contact layers. LED's using the SLS active region generally exhibited the brightest electroluminescence. At 300K, the best SLS-LED emitted at 4.1μm with 80μW of average power at 200mA of average current.

The p-n junction SLS-LED's consisted of 17 periods of undoped (n-type) material followed by 3 periods and an InAs contact layer doped with zinc. With increasing levels of zinc doping the PL intensity decreased. Without heterobarriers to provide additional electron confinement, the LED emission at 300K is significantly weaker than the other device structures tested. (Figure 6) The addition of an p-AlAsSb heterobarrier greatly improved LED emission by confining electrons to the active region.

The initial multi-stage devices were resistive and performed poorly. The addition of a AlGaAsSb grade between the AlAsSb heterobarrier and the GaAsSb used in the semi-metal injector improved the hole transport through the structure. This lowered the resistance and resulted in our best performing devices. Other schemes to improve hole transport at the AlAsSb-GaAsSb interface also had the same effect as the AlGaAsSb grade. The best performing multi-stage device consisted of 10 stages each with 5 periods of SLS as the active region. The LED emission of a 10 stage - 3 period SLS is also shown in Figure 6. At 80K, the 10 stage - 5 period device emitted at 3.7μm with 2.4mW (200mA) and at 300K with 100μW (200mA) at 4.2μm. (Figure 7.)

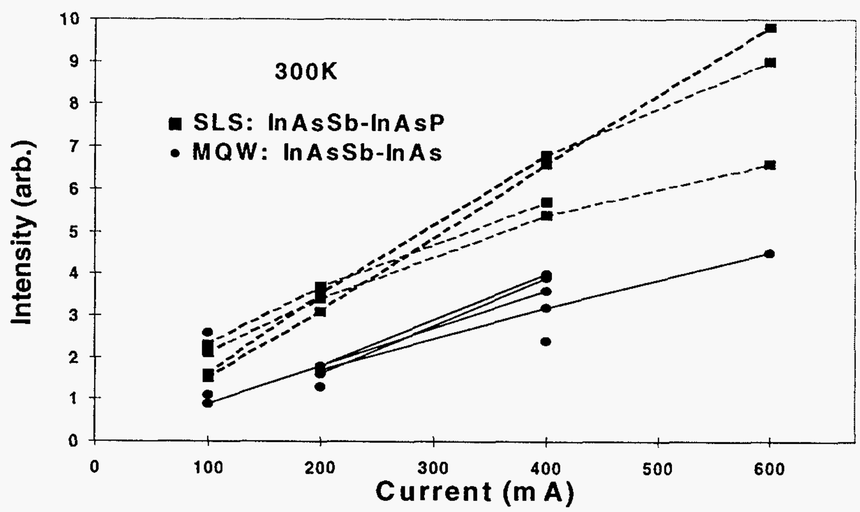

Figure 5. LED emission from devices using AlAsSb heterobarriers at 300K versus peak current measured. LED's with (■) SLS active regions typically had better performance than devices with (•) MQW active regions. Measurements were made at 1KHz with a 50% duty cycle.

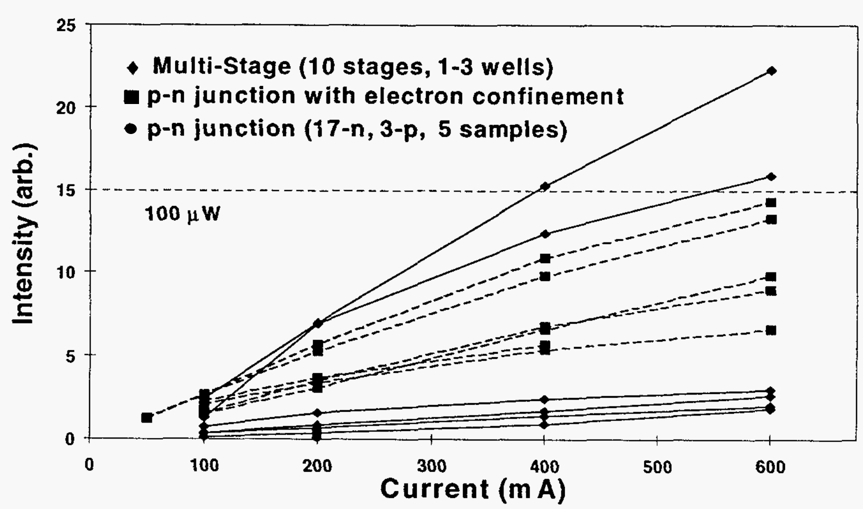

Figure 6. Multi-stage LED's initially performed poorly but improvements in hole transport within each stage resulted in devices with the brightest LED emission measured in this work. LED emission intensity measured from (•) p-n junction LED's are between .5 to 1 (arb. units) at 200mA and are not well resolved in this plot.

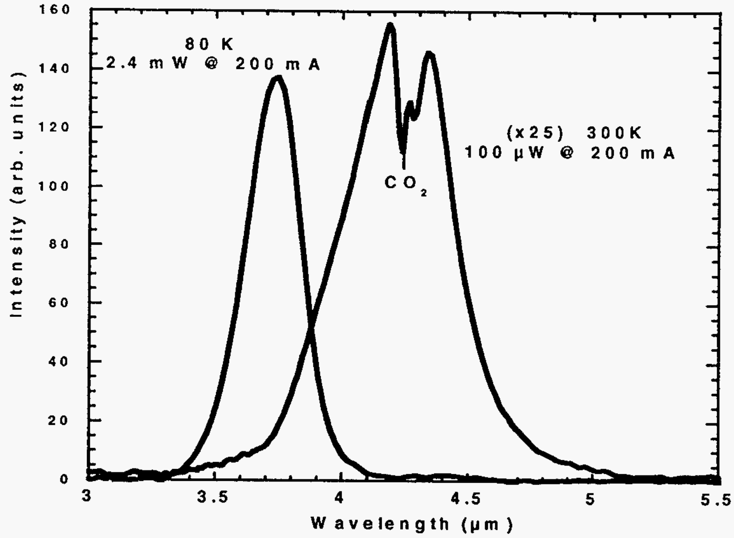

Figure 7. LED emission at 80K and 300K from a 10 stage - 5 period SLS-LED.

A room temperature CO_2 sensor system was setup to investigate the viability of using LED's in a gas sensor system. The system consisted of a LED emitting at 4.2μm with 100μW of total power. The LED was mounted on a TO-3 header with a parabolic reflector to help improve collection efficiency. The diode was modulated at 2KHz. The LED emission was passed through a beam splitter to a 8cm gas cell and a reference path.. The reference beam was chopped at 100Hz. The signals were recombined and detected using a single PbTe detector. Using three lock-in amplifiers to compensate for thermal drift of the LED and detector, we obtained the signal shown in Figure 8. Concentrations of CO_2 in N_2 decreased from 100ppm to 24ppm with N_2 purges. Significant improvements in sensitivity are expected by improving the optical coupling between the LED and gas cell using front surface emitting LED's and with improved thermal stability.

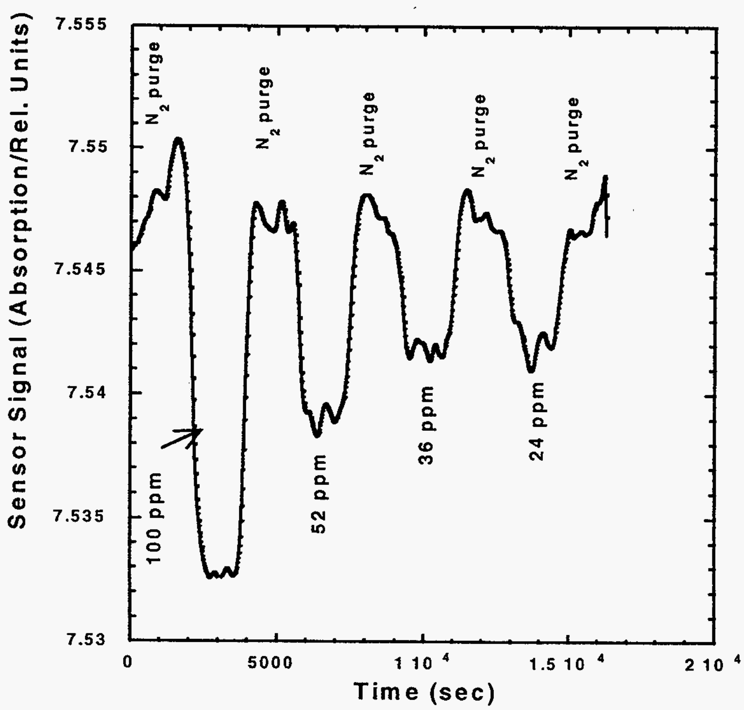

Figure 8. Measurements of CO_2 in N_2 using a first generation sensor system with an InAsSb based LED.

6. SUMMARY

We have fabricated light emitting diodes employing either InAs-InAsSb MQW or InAsP-InAsSb SLS structures as the active region. The growth of these active regions are sensitive to the growth conditions during the interface transition. LED's with SLS active regions typically had brighter electroluminescence. At 300K, we measured an average power of 80μW (200mA) at 4.1μm for SLS devices using an AlAsSb heterobarrier for electron confinement. We have demonstrated multi-stage LED devices which employ a n-InAs/p-GaAsSb semi-metal interface between each stage for carrier injection. A 10 stage device consisting of 5 periods of a SLS active region exhibited 300K emission exceeding 100μW (200mA) at 4.2μm. A simple CO_2 sensor system was demonstrated with sensitivity of 24ppm with a 8cm path length.

7. ACKNOWLEDGEMENTS

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