

## Mid-IR III-V Semiconductor Diode Lasers for Trace Gas Monitoring

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### ABSTRACT

The development of mid-IR III-V semiconductor diode lasers is briefly reviewed. Particularly, the recent progress and current status of Sb-based type-II interband cascade lasers are presented. How these diode lasers can be developed to meet the application requirements in chemical sensing is discussed.

### INTRODUCTION

It is widely recognized that the development of compact and efficient mid-IR (3-12  $\mu\text{m}$ ) sources would dramatically enhance chemical sensing capabilities since many gases of technological interest exhibit their fundamental absorption lines in this wavelength range. Examples of these include  $\text{CH}_4$  (3.3  $\mu\text{m}$ ),  $\text{CO}_2$  (4.2  $\mu\text{m}$ ),  $\text{CO}$  (4.6  $\mu\text{m}$ ), and  $\text{NO}$  (5.3  $\mu\text{m}$ ). Though weaker overtone transitions in the 1-2 micron region also exist for some of these molecules, the stronger absorption lines in the mid-IR would permit monitoring of a wider range of gases with improved detection sensitivity. Table 1 lists the detection limits for some important species, showing orders of magnitude improvement in sensitivity [1] by using mid-IR lasers compared to near-IR diode lasers.

**Table 1. Detection limits using diode laser spectroscopy**

species	<i>ppb</i>	mid-IR ( $\lambda$ )	<i>ppb</i>	Near-IR ( $\lambda$ )
$\text{H}_2\text{O}$	2.0	5.94 $\mu\text{m}$	60	1.39 $\mu\text{m}$
$\text{CO}_2$	0.13	4.23 $\mu\text{m}$	3000	1.96 $\mu\text{m}$
$\text{CO}$	0.75	4.6 $\mu\text{m}$	500	2.33 $\mu\text{m}$
$\text{NO}$	5.8	5.25 $\mu\text{m}$	60000	1.8 $\mu\text{m}$
$\text{CH}_4$	1.7	3.26 $\mu\text{m}$	600	1.65 $\mu\text{m}$
$\text{HCl}$	0.83	3.4 $\mu\text{m}$	150	1.79 $\mu\text{m}$
$\text{H}_2\text{OC}$	8.4	3.55 $\mu\text{m}$	50000	1.93 $\mu\text{m}$
$\text{NH}_3$	0.8	10.3 $\mu\text{m}$	800	1.5 $\mu\text{m}$

Because of combined advantages in terms of cost, volume, weight, simplicity of design, reliability, remote sensing capability, fast response, high sensitivity, and selectivity, semiconductor laser

spectroscopic gas analyzers in this wavelength range are very desirable. However, their broad application is currently limited by a lack of adequate IR laser sources. Requirements for such lasers include a relatively high output power (ranging from the mW to Watts levels depending on specific applications) and continuous wave (cw) operation either at ambient temperature or at temperatures accessible with thermoelectric (TE) coolers. Here, the development and status of mid-IR III-V semiconductor diode lasers, particularly emerging interband cascade lasers, are reviewed for assessing how these diode lasers can be advanced to meet the application requirements.

### CONVENTIONAL DIODE LASERS

The emission wavelength  $\lambda$  (in  $\mu\text{m}$ ) of conventional semiconductor lasers available today is mainly in the visible and near-IR ( $\lambda < 2 \mu\text{m}$ ), which is essentially determined by the band-gap  $E_g$  (in eV) of semiconductor material in the active region with an approximate relation of  $\lambda \approx 1.24/E_g$ . For visible and near-IR wavelengths, mature diode laser technology has been established based on GaAs-family (lattice constants near 5.7  $\text{\AA}$ ) and InP-family (lattice constants near 5.9  $\text{\AA}$ ) heterostructures with efforts over several decades and with wide range of applications especially in optical-fiber communication and data storage. The InP-based diode lasers have been mainly focused on the most important wavelength range today, i.e. 1.3 and 1.55  $\mu\text{m}$ , where silica fibers exhibit the lowest losses. Although InP-based diode lasers beyond 1.6  $\mu\text{m}$  have shown good performance [2-3], their commercial sales are negligible in the overall market and thus the InP-based diode laser manufacturers are much less interested in making these longer wavelength diode lasers. Due to the inherent band-gap constraint of materials that can be used with acceptable strain, the longest wavelength of InP-based diode lasers reported was about 2.2  $\mu\text{m}$  [4] and has not been able to reach mid-IR wavelength range where the fundamental absorption lines of gases are located.

To extend diode lasers into mid-IR wavelength range, three narrow band-gap material systems – i.e., the IV-VI lead salts, the II-VI ternary alloys, and the Sb-based III-V compounds– have been used in the conventional interband transition approach. Of these, the lead salt diode lasers have been commercially available for many years with a main application in high sensitivity gas analyses [5]; however, due to poor thermal conductivity and high susceptibility to damage, their output power is typically lower than 1 mW with cw operating temperatures below 223 K. While the II-VI materials (e.g. HgCdTe) have been used extensively for IR detection from 2 to over 20  $\mu\text{m}$ , their development for mid-IR lasers is much less advanced than other semiconductor systems such as lead salts and Sb-based III-Vs.

The Sb-based type-I heterostructure lasers (lattice constants near 6.1  $\text{\AA}$ ) have been under considerable investigations and have achieved steady progress in recent years with good cw performance at room temperature at wavelength range of 1.9 to 2.7  $\mu\text{m}$  [6-9]. However, the development of diode lasers with non-cryogenic operating temperatures and relatively high output powers at mid-IR ( $>3 \mu\text{m}$ ) wavelengths has proven to be much more challenging due to some inherent difficulties. The maximum operating temperature of these Sb-based mid-IR lasers is not higher than 255 K and 175 K under pulsed and cw conditions, respectively. The inherent difficulties include (1) losses due to the non-radiative Auger recombination process, which increasingly predominates when the temperature is raised and the energy gap lowered for longer-wavelength emission, (2) inadequate electrical confinement due to small conduction and/or valence band offsets, (3) poor efficiency in utilizing applied bias voltage for the small photon energy, (4) increased optical absorption loss with longer wavelengths, and (5) the non-uniform distribution of injected carriers. Also, because of the type-I nature of these diode lasers, the lasing wavelength is constrained to the band-gap of the material and the further longer wavelength ( $>5 \mu\text{m}$ ) lasers have to use a very narrow-gap III-V compound InSb (lattice constants near 6.5  $\text{\AA}$ ) [10] with cryogenic operating temperatures.

## EMERGING SEMICONDUCTOR LASERS

A new approach, utilizing intersubband transitions in artificial semiconductor quantum well (QW) structures [11-12] for mid-IR lasers, is represented by intraband quantum cascade (QC) lasers [13] based on a staircase of coupled AlInAs/GaInAs QWs first

demonstrated in 1994. The wavelength of intraband QC lasers is determined by the small energy separation of conduction subbands arising from quantum confinement in QW structures (Fig. 1) based on wider band-gap semiconductor materials. Hence, the lasing wavelength can be tailored in principle over a wide spectral range from the mid-IR to far-IR region by merely changing the QW layer thickness. Another distinct feature of the QC laser is that each injected electron is reused to possibly generate an additional photon as it cascades down each step of the energy staircase, leading to quantum efficiency greater than the conventional limit of unity, desirable for obtaining high output power. Rapid advances have been made in InP-based QC lasers with wavelengths ranging from 3.5 to 24  $\mu\text{m}$ , single mode operation with distributed feedback (DFB), peak power levels in the Watts range and above-room-temperature pulsed operation for wavelengths from 4.5 to 16  $\mu\text{m}$  [14]. Progress has also been made in GaAs-based QC lasers with wavelength range of 7-13  $\mu\text{m}$  and room-temperature pulsed operation at wavelengths of  $\sim 9$  and 12.6  $\mu\text{m}$  [15-16].

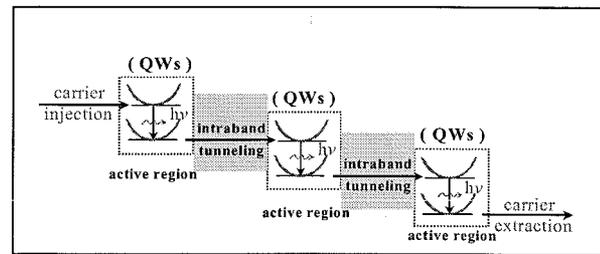


Fig. 1. Illustration of intraband QC lasers

As shown in Fig. 1, the two transition subbands in an intraband QC laser have nearly parallel dispersion curves in energy-momentum space such that the relaxation between them is dominated by a very fast phonon scattering. Consequently, intraband QC lasers have relatively high threshold current densities (typically  $>1 \text{ kA/cm}^2$ ), leading to significant heating and limiting power (wall-plug efficiency  $\leq 10\%$ ). On the other hand, their threshold current densities have weak temperature dependence due to fast phonon scattering rate and that the material gain is much less sensitive to the thermal broadening of the electron distributions for two nearly parallel subbands. The maximum pulsed operation temperatures exceeding 400 K was reported in the wavelengths from 5.5 to 11.2  $\mu\text{m}$  [17-20]. Because of a considerable amount of heat generated in the active region, cw operating temperature was limited to 175 K and 10 K for InP-based and GaAs-based QC lasers, respectively. It is

challenging for intraband QC lasers to achieve cw operation with high output power at room temperature. Nevertheless, with constant and extensive efforts in improving laser design and fabrication, the cw operation at room temperature was reported most recently for a InP-based QC laser at a wavelength of  $\sim 9 \mu\text{m}$  [21].

Though the emission wavelength of QC lasers is essentially controlled by the QW geometry, its wavelength coverage is practically limited on the short side to a fraction of the relevant band offsets of the materials used. For this reason, the QC laser performance decreases when the wavelength is shorter than  $\sim 5 \mu\text{m}$  due to the limited band offset ( $\sim 0.52 \text{ eV}$ ) in the InGaAs/InAlAs/InP system (responsible for significant reductions in carrier injection efficiency and population inversion). In principle, employing strain-compensated InGaAs/InAlAs/InP structures with increased conduction band offset (or using other materials) can extend the intraband QC lasers to better cover the 3-5  $\mu\text{m}$  range, which has been reported [22-24]. However, the shorter wavelength QC laser performance comparable to the longer wavelength QC lasers remains to be proved.

Type-II GaInSb/InAs superlattice (SL) and QW structures have been explored in recent years for mid-IR lasers [25-26] with possible suppression of non-radiative Auger recombination. The band-gap of a type-II SL is determined by the energy separation between the first conduction miniband and the top-most heavy-hole miniband, rather than the band-gap of a constituent material. Hence, the SL structure can, in principle, be tailored by adjusting constituent layer thicknesses and compositions to cover a wide wavelength range. Optical-pumping has yielded impressive results, indicative of the suitability and potential of this type-II QW system for lasers. Recently, type-II W QW diode lasers at a wavelength of  $\sim 3.25 \mu\text{m}$  have been demonstrated at temperatures up to 310 K and 195 K under pulsed and cw conditions, respectively [27]. However, since the conventional  $p$ - $n$  junction diode structure with the traditional carrier injection scheme is retained in these laser devices, they do not reuse injected carriers for sequential photon emission as in the type-I QC lasers. In the mid-IR wavelengths, where the voltage drops across the active region may be a small fraction of the total bias and the current-crowding effects (such as nonuniform current distribution and band-filling) will be more severe, their output power, cw operation temperature, and power efficiency may not be high enough to meet application requirements. These

difficulties can be significantly alleviated using the novel approach of interband cascade (IC) lasers.

The concept of IC lasers was first proposed in 1994 [28] and is illustrated in Fig. 2. Using interband tunneling facilitated by the broken band-gap alignment in type-II QWs, IC lasers reuse injected electrons and form cascaded interband transitions for multiple photon generation, leading to a quantum efficiency significantly greater than the conventional limit of unity, similar to the intraband QC laser. Using optical transitions between the conduction and valence bands with opposite dispersion curvatures, IC lasers circumvent the fast phonon scattering loss in intraband QC lasers and possess a wide wavelength tailoring range that is less limited by the conduction-band offset on the short wavelength side.

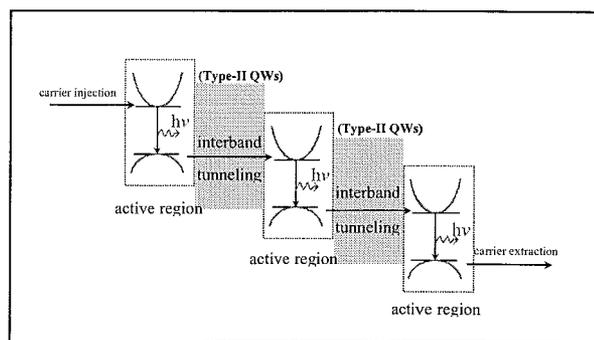


Fig.2. Illustration of the type-II IC laser concept

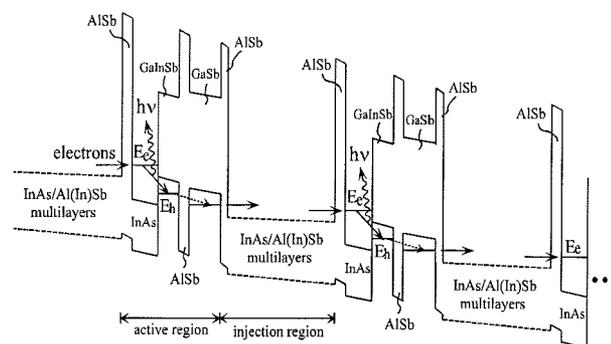


Fig.3. Schematic band diagram of a type-II IC laser structure

Type-II IC lasers can be constructed from the nearly lattice-matched InAs/GaSb/AlSb III-V material system [28], which takes advantage of their characteristic type-II band-edge alignments. The IC laser concept is flexible and many variations/refinements on IC laser configurations are possible [29-30]. The band diagram of a typical type-II IC laser structure under a forward bias is shown in Fig. 3, where repeated active regions are separated by

*n*-type doped injection regions consisting of digitally graded InAs/Al(In)Sb multilayers. The active regions comprise InAs/GaInSb type-II QWs, where optical interband transitions occur and Auger recombination can be suppressed through band-structure engineering [31-33]. The electrons injected from an injection region to the level  $E_c$  are effectively blocked from directly tunneling out by the GaInSb, AlSb and GaSb layers, minimizing leakage current. These properties make it possible for mid-IR IC lasers based on InAs/GaInSb type-II QWs to operate efficiently with low threshold current density at relatively high temperatures in cw modes and to deliver high output powers.

By combining the advantages of quantum cascade lasers and type-II quantum well interband lasers, theoretical simulations [29, 34] project the feasibility of IC lasers operating in cw mode up to room temperature with high output powers. Significant advances toward such a high performance have been reported [35-40] in terms of record-high differential external quantum efficiency (>600%), peak output power (~6 W/facet at 80 K), cw power conversion efficiency (>16% at 80 K), and room temperature operation under pulsed conditions.

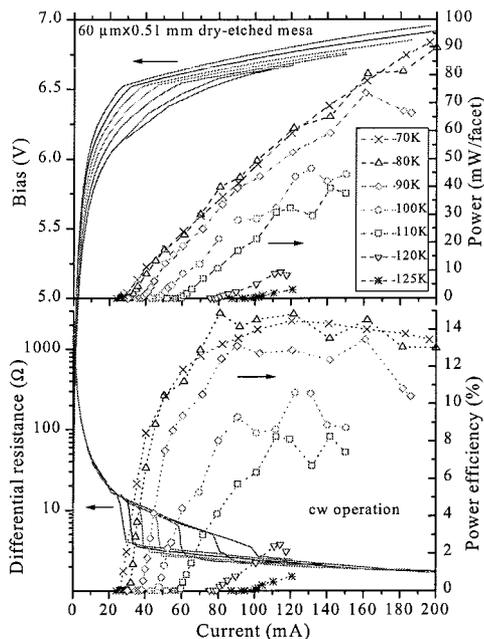


Fig. 4. *I-V-L* characteristics, differential resistance and power efficiency for a 60- $\mu\text{m}$   $\times$  0.51-mm dry-etched mesa-stripe laser

Figure 4 shows the *I-V-L* characteristics, power efficiency and differential resistance for a 60- $\mu\text{m}$ -wide dry-etched mesa-stripe IC laser [36] under cw conditions at heat sink temperatures ranging from 70 to 125 K. The average differential external quantum efficiency exceeded 300% at 70 and 80 K with an output power of ~90 mW/facet at a current of 200 mA. Hence, a type-II IC laser can deliver considerable power at a low current in contrast to other types of mid-IR diode lasers. Significant slope changes of the *I-V* characteristic curves were observed, corresponding to an abrupt reduction of differential resistance at the threshold as shown in Fig. 4. The differential resistance was initially very high (>10 k $\Omega$ ), suggesting good material quality with insignificant leakage. The abrupt reduction of differential resistance at the threshold clearly manifested the start-up of lasing action associated with a rapid increase in the pace of carrier transport around threshold. Power efficiencies (>14%) among mid-IR diode lasers were obtained from this device at 70 and 80 K.

## CURRENT STATUS AND CHALLENGES

To give an overview of the current status of mid-IR III-V diode lasers, Fig. 5 and Fig. 6 show the maximum operating temperature and output power as a function of wavelength, respectively, for various Sb-based diode lasers, compiled from the literature [6-10, 25-27, 35-40]. Fig. 7 shows the maximum operating temperature of intraband QC lasers [13-24].

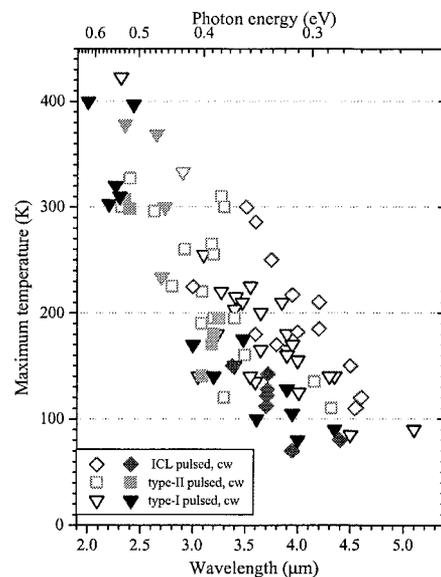


Fig. 5. Reported maximum temperature vs. wavelength for mid-IR III-V Sb-based interband diode lasers

While the non-cascade diode lasers still exhibit better values for shorter wavelengths ( $\sim 2\text{-}3.3\ \mu\text{m}$ ), for the longer wavelengths ( $\sim 3\text{-}5\ \mu\text{m}$ ), type-II IC lasers appear to become the preferred type in terms of operating temperature and output power, as well as power efficiency for the reasons discussed and the results demonstrated already. Considering significant room for improvement, extended wavelength coverage with superior performance is certainly possible for type-II IC lasers. However, it is premature to project where the boundaries can be drawn until further investigations are undertaken in the longer and shorter wavelength regions.

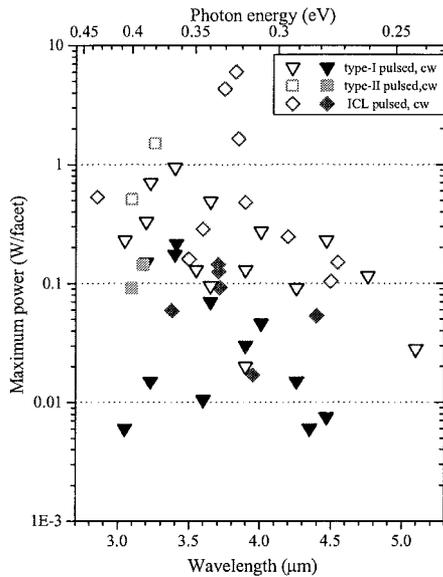


Fig. 6. Reported maximum output power vs. wavelength for mid-IR III-V Sb-based interband diode lasers

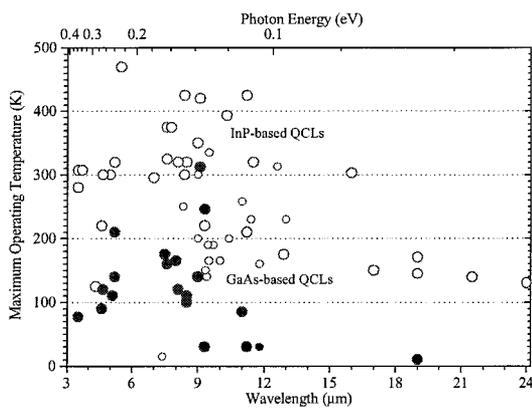


Fig. 7. Reported maximum operating temperature vs. wavelength for intraband QC lasers. Open and solid circles (large for InP-based and small for GaAs-based QC lasers) are for pulsed and cw modes, respectively.

In the long-wavelength ( $>5\ \mu\text{m}$ ) region, QC lasers have achieved impressive performance superior to other types of diode lasers. Many practical applications are viable with the use of intraband QC lasers in the wavelength range and are expected to replace lead salt lasers in some commercial market. In the  $3\text{-}5\ \mu\text{m}$  wavelength region, type-II IC lasers are very promising to fill the gap between the conventional diode lasers and intraband QC lasers. An IC laser operated at 300 K at wavelength of  $3.51\ \mu\text{m}$  [40], demonstrating the first room-temperature interband diode laser beyond  $3.5\ \mu\text{m}$ . Under pulsed conditions, type-II IC lasers exhibited the record-high peak powers (e.g.  $\sim 6\text{W}/\text{facet}$ ) among mid-IR, showing their great potential to deliver high output powers demanded for remote sensing and lidar applications. However, the performance of type-II IC lasers under cw conditions has not shown as much advantage as theories [29,34] have predicted. CW output power in the 100 mW level can be obtained at low temperatures (e.g. 80 K). But, the maximum cw operating temperature is currently no higher than 150 K [40]. This is due mainly to large thermal resistance in present type-II IC lasers. Thermal resistance could be reduced significantly through optimizing device fabrication and packaging. Another approach is to look for optimum crystal growth conditions and to reduce interface roughness in order to minimize losses. The growth of Sb-based lasers and thus their performance are significantly affected by the quality of commercially available GaSb substrates, which is considerably inferior to that of GaAs and InP substrates and presents a challenge to the consistent growth of high-quality lasers. The improvement of the quality of GaSb substrates as well as the polishing and cleaning techniques will enhance the performance of these mid-IR lasers and their reliability.

Although recent IC lasers have demonstrated with very low threshold current densities at low temperatures (e.g.  $\sim 13\ \text{A}/\text{cm}^2$  at 80 K [40]), the threshold current densities at higher temperatures are still substantially larger than they need to be. Designing laser structures that suppress various loss mechanisms at high temperatures is challenging due to uncertainties/inaccuracies of some material parameters and the difficulty of incorporating the effects of interface roughness. Therefore, extensive investigations for improving the material quality and deepening our understanding of the underlying physics are needed to raise type-II IC laser performance to levels necessary for fulfilling application requirements

such as cw operation at room temperature. Future work should cover more detailed aspects for optimizing the laser design, MBE growth, material quality, and the development of advanced processing and passivation techniques for Sb-based heterostructure devices. Other directions include integrating conventional distributed feedback (DFB) and two-dimensional photonic-crystal gratings into type-II IC lasers to address applications requiring high spectral purity and improved beam quality. Also, vertical cavity surface emitting lasers based on type-II IC structures remain largely unexplored and may yet prove to be a desirable mid-IR source, while the intraband QC lasers are constrained to edge-emission in the transverse magnetic (TM) mode.

### CONCLUDING REMARKS

New mid-IR diode lasers based on III-V semiconductors have been emerged with remarkable progress. InP-based intraband QC lasers appear to be ready for immediate applications in the long-wavelength IR region ( $>5 \mu\text{m}$ ) at ambient environments. This great achievement can be attributed largely not only to the advancement of device physics, but also to tremendous investment and extensive efforts on InP-related technologies over several decades. Compared to InP- and GaAs-based materials and relevant technologies, Sb-based materials and device structures are much less explored. However, Sb-based type-II IC lasers have progressed with very encouraging results in the first IR transmission atmospheric window region (3-5  $\mu\text{m}$ ) where the fundamental absorption lines of many important gases are located. Considering less mature materials and imperfect device processing/fabrication technologies, as well as very limited investments, type-II IC lasers are still on an early stage and there is a significant room for improvement. One can expect that, with continued and expanded efforts and more supports, the development of type-II IC lasers will be accelerated to meet application requirements in many areas such as chemical sensing and environmental monitoring.

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