Quantum Cascade Lasers Tuned by Amorphous As₂S₃ Claddings

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ABSTRACT

Quantum cascade lasers (QCLs) have become a key component in the development of optical approaches to sensing applications. Recent experiments have shown the ability to achieve second harmonic generation from these structures suggesting the possibility of achieving short wave-infrared output. However, in these cases the power of the non-linear mode is limited by its phase mismatch with the fundamental cavity mode. By modifying the effective index of the laser system through cladding, one may ameliorate the mismatch to increase power output. In this study, we develop a simple method for drop-coating arsenic sulfide (As₂S₃) glass on QCLs. The glass is processed by above band-gap illumination, which induces a change in the refractive index resulting in a shift of the output mode of the laser. We observe the effective index to change by a factor 1.3×10^{-4} after 20 minutes of illumination at 312 nm for the fundamental wavelength of the QCL. Below band-gap irradiation, such as that occurring during device operation, is confirmed to have no effect on the material. Studies of the output of QCLs reveal for the first time mode shifting of the spectra as a result of optical modification to a cladding layer.

Keywords: chalcogenide glass, quantum cascade laser, QCL, laser processing, arsenic sulfide, second harmonic generation

1. INTRODUCTION

Quantum Cascade Lasers (QCLs) have been the focus of much investigation over the past decade because of their many desirable properties. They can be operated in both continuous and pulsed mode with higher performance than traditional semiconductor lasers at the same wavelength. Pulsed operation can be achieved over a broad range of temperatures, with pulse lengths on the order of picoseconds and repetition rates as high as 10 GHz. Lastly, QCLs can be made to produce light with a wavelength anywhere between 3.5 and 24 μm , with pulsed operation in the range of 4.5 to 16 μm possible at room temperature [1].

The ability of QCLs to produce light anywhere in the mid- to far-infrared range (roughly 5-20 μm) makes them a natural choice for trace gas sensing. The spectroscopic fingerprints of many interesting trace gasses such as the byproducts of fossil fuel burning and the components of human breath lie in the mid-infrared range. For this reason, these gasses are difficult to detect using traditional semiconductor lasers, the output of which tends to be limited to the visible and near-infrared ($< 2 \mu\text{m}$). The output range of QCLs provides a natural solution to this problem. Trace gas sensing has thus been the main application for which QCLs have been tested, with diverse groups reporting a plethora of methods for the sensing of specific gasses. Several recent efforts have shown sensitivities to parts per billion [1].

If the output range of QCLs could be extended to shorter wavelengths, their high bandwidth could lead to a host of new applications. Although the limitations of existing semiconductor materials make it unlikely that the methods currently used to customize the output of a QCL could be utilized to produce this relatively short wavelength [1], it may be possible to reach it via second harmonic generation (SHG) [2]. Additionally, by pushing the output range of QCLs to the short wave-infrared range, one can take advantage of the beneficial properties of QCLs in replacing existing semiconductor laser technology.

Currently, the second harmonic power output of appropriately designed QCLs is a tiny fraction of their output

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at their fundamental frequency. It may be possible to dramatically increase output at the second harmonic by placing a cladding on the laser. Such a cladding would need to be relatively easy to apply and process on a QCL without impeding the laser's operation or degrading over time. The cladding would need change the output spectrum of the QCL at both the fundamental and second harmonic so as to reduce the difference in effective index experienced by the two waveguide modes. Finally, the cladding would need to have optical properties that could be precisely and permanently modified after application to facilitate the tuning of individual lasers.

In this paper, arsenic sulfide (As_2S_3) is deposited through solvent casting as a cladding for QCLs. The unimpeded functioning of a QCL coated with As_2S_3 using this method is demonstrated and shown to persist over long periods of operation. We observe a frequency shift in the QCL output after optically modifying the active cladding material with above band gap illumination and suggest a change in the effective index of refraction as its cause.

2. BACKGROUND

Quantum cascade lasers (QCLs), first demonstrated in 1994 by Faist et al. [3], retain all of the advantages of a mid-infrared quantum well laser with significantly improved power and temperature performance. A QCL essentially consists of a series of quantum wells of varying widths. Rather than use interband transitions between valence and conduction bands, QCLs rely on intersubband transitions, i.e. transitions within the conduction band which give them several advantages over double heterostructure and quantum well lasers. In a typical QCL each electron contributes 20-50 photons instead of the one it would produce in a double heterostructure or quantum well laser. QCLs thus exhibit high optical power.

The dependence of QCLs on intersubband transitions comes with a price. It is unlikely that any amount of bandgap engineering of conventional III-V materials (GaAs- or InP-based heterostructures) will be able to produce a QCL with a laser transition large enough to emit photons at $1.55 \mu\text{m}$ (0.8 eV), the main wavelength for telecommunications [2], or even in the $2 - 4 \mu\text{m}$ range. Since the high-speed properties of QCLs mentioned above would make them excellent for use in this field, it is worthwhile to explore other ways to have QCLs produce short wave-infrared light. A particularly promising method is second harmonic generation.

In 2003, a QCL was demonstrated with a large $\chi^{(2)}$ in the direction of laser propagation. This internal approach to SHG was a major improvement over previous attempts at SHG in a QCL, which relied on a nonlinear crystal external to the laser and thus suffered significant interface losses [2]. Theoretical calculations done as part of this previous experiment found that for a QCL of cavity length L the phase matching condition is

$$I^{(2\omega)} \propto \frac{1 + e^{-2\alpha_2 L} - 2e^{-\alpha_2 L} \cos(\Delta k_\omega L)}{(\Delta k_\omega^2 + \alpha_2^2)}, \quad (1)$$

where α_2 represents the total loss of a cavity mode at the second harmonic and Δk_ω is the phase mismatch defined as

$$\Delta k_\omega = k_{2\omega} - 2k_\omega = \frac{2\omega}{c}(\mu_{2\omega} - \mu_\omega) \quad (2)$$

with $k_{2\omega}$ and k_ω the wavenumbers and $\mu_{2\omega}$ and μ_ω the effective indices of refraction at the second harmonic and fundamental respectively. As expected, it is evident from equation 1 that $I^{(2\omega)}$ reaches a maximum when $\Delta k_\omega = 0$. It was also found that the phase mismatch was 100 times larger than the modal losses α_2 . For this reason, achieving or even approaching perfect phase matching could increase power output at the second harmonic by two orders of magnitude. Such an improvement is required before second harmonic generating QCLs could be used in practical applications.

One possible way to improve phase matching would be to coat a QCL with a cladding chosen to reduce $\mu_{20} - \mu_0$. This is possible because the waveguide modes have a non-negligible tail extending outside of the QCL into the environment [4]. By placing a coating on the sides of the QCL, one should be able to modify the waveguide loss and should be able to change the index of refraction seen by that tail. Thus, by continuity of the wavefunction, the effective index seen by the mode itself will be tailored. We study arsenic sulfide (As_2S_3) as an appropriate cladding material for this application.

Arsenic sulfide first attracted attention in the early 1970s when it was discovered that thin films of As_2S_3 darkened significantly under illumination [5]. As_2S_3 was first considered as a material for photography and then as a potential photoresist, with methods for spin coating it and studies of the properties of spun films appearing in the early 1980s [6-8]. Studies of the dependence of the optical properties of spin-coated As_2S_3 films on illumination soon followed [9, 10]. Particularly interesting is that the index of refraction was found to depend strongly on wavelength [11] and to permanently increase by several percent after illumination [12, 13].

In this study we present a simple solvent casting method for the deposition of As_2S_3 cladding on a QCL. After processing, the QCL continues to function over extended periods. The cladding is modified by above band gap illumination, which increases the effective index of refraction and causes a measurable change in the laser's output spectrum.

3. PROCEDURE

Bulk As_2S_3 (Cerac) crystals were ground into a fine orange powder using a mortar and pestle. $2.68 \pm .03$ gm of the powder was then combined with $6.24 \pm .03$ gm (approximately 10 ml) of butylamine (Aldrich) and allowed to dissolve for several days. Beginning immediately after mixing and continuing throughout the experiment, exposure of solution or samples to ambient light and atmospheric moisture was kept to a minimum.

Figure 1: Cartoon of chalcogenide glass cladding on quantum cascade laser before and after illumination

Figure 1 shows a cartoon of a QCL ridge cross-section with chalcogenide glass cladding. The QCLs were processed and mounted to a copper holder; wire bonding to the ridge was used for electrical contacts. Using a pipette, we then applied approximately 10-50 μL of solution onto a bar of 5-10 lasers. The mounted QCLs were baked in a vacuum oven for 30 minutes at 80 $^{\circ}\text{C}$ allowing the butylamine to evaporate out of the films [6]. QCLs were then examined using optical microscopy. Figure 2 shows the QCL before and after cladding indicating that this method was able to produce a complete and even coating.

The QCLs were operated in pulsed mode at room temperature under different processing conditions and the output spectrum at the fundamental frequency was recorded directly by an FT-IR spectrometer (Nicolet). Typical input currents of 2-3 A, 100 ns pulse lengths, and a driving frequency of 80 kHz were used. Above band-gap illumination was provided by a Fotodyne FOTO/UV 300 Ultraviolet Transilluminator with four 312 nm bulbs rated at 15 W. Measurements were taken at discrete intervals of 10 and 20 minutes of illumination with the sample removed from the stage during illumination. For below band-gap illumination, a 50mW rated 650 nm diode laser was employed.

However in this case, the sample was illuminated in place and spectra were acquired continually. Data is represented as a function wavelength and wavenumber after background subtraction. Table I shows the measurement conditions for this experiment.

Figure 2: Optical micrographs of QCLs before (left) and after (right) cladding with As_2S_3 glass.

Coating	Input Current (A)	Illumination	Measurement Times
No	2	None	Every 10 mins for 6 hrs
Yes	2	None	Every 10 mins for 6 hrs
Yes	2	650 nm	Every 10 mins for 5 hrs
Yes	3	312 nm	After 0, 10, and 20 mins of illumination

Table 1: Summary of conditions under which the output of QCLs was measured.

4. RESULTS

Figure 3 shows the output spectrum of a QCL before and after the cladding is applied. The observed behavior on the unclad laser is consistent with previous results for QCLs [1]. Once the chalcogenide glass is applied and processed, we observe similar mode structure indicating our deposition and baking process is not detrimental to the QCL. Detailed lifetime measurements of the laser were not acquired, although we did not observe premature device failure over the course of the experiment.

Based on the data in Figure 3, we observe a decrease in the absolute output power after the As_2S_3 has been added. We believe that this is a result of excess solution leaking onto the front of the laser modifying the properties of the cavity mirror. This problem can be easily remedied by using a more controlled solution application through direct-write techniques such as ink jet [14] or laser direct-write techniques [15]. More significantly, a substantial shift was observed in both the main and secondary output peaks. It is not clear whether this is the result of the physical presence of the As_2S_3 on the front of the laser, which could lengthen the optical cavity, or the change in the effective index of refraction at the fundamental due to the As_2S_3 on the sides of the QCL or both. Additional studies are required to isolate these effects.

The changes in output caused by above band gap illumination are clearly illustrated in Figure 4. Ten minutes of cw UV exposure at 312 nm caused a significant shift and power increase in the main output peak of the coated QCL and a substantial change to the positions and relative heights of the secondary peaks as compared with the pre-illumination spectrum. Additional illumination for another 10 minutes results in additional shift in the peak locations, but to a lesser extent. The measurements were all taken within a span of time short enough to avoid any major fluctuations in the laboratory conditions. We thus infer that this alteration in the spectra is the result of a photoinduced change in the optical properties of As_2S_3 .

Figure 3: Comparison of the output spectra of a QCL before and after coating with As_2S_3 . There is a clear shift in peak position after the cladding is applied.

Figure 4: Comparison between the output spectra of a coated QCL before illumination and then after 10 and 20 minutes

of exposure to 312 nm UV light. A shift in peak positions was observed after 10 minutes of illumination. A marked increase in the height of the main peak observed after 10 minutes appeared to have continued during a second 10 minutes of illumination although peak positions seemed to stabilize.

The results of Figure 4 can be quantified more completely by calculating the change in effective index that would produce such a shift in mode structure. Based on the definition of the index of refraction,

$$\frac{\Delta\mu}{\mu} \equiv \frac{\mu' - \mu}{\mu} = \frac{\Delta k}{k},$$

where in this case, Δk is defined as the shift in wavenumber as a function of illumination time.

Figure 5: Magnification of data shown in figure 4 with wavelength converted to wavenumber.

A close-up of the output spectra over five mode peaks is shown in Figure 5. The data is represented as a function of wavenumber to highlight the change in index, described by equation 3. As the illumination time increases, there is a shift in the data to higher wavenumbers corresponding to higher effective index. Over the five peaks shown, average Δk of 0.11 cm^{-1} after 10 minutes and 0.15 cm^{-1} after 20 minutes are obtained. These shifts are normalized to obtain a change in effective index of 9.5×10^{-5} and 1.2×10^{-4} respectively. The measured change in index is significantly lower than one might expect for the pure chalcogenide glass [12,13]. However, since only a small portion of the propagating wavefunction leaks into the cladding region, we would expect the effective index to change by only a fraction of the index change of the glass itself. Further studies are needed to independently measure the change in the cladding.

The QCL output spectrum is found to stay constant under sub-bandgap illumination. The modes of the clad laser remain unchanged from the uncoated sample as shown in figure 6 after five hours of laser operation and illumination at 650 nm. Although the spectra are taken at lower resolution, we notice that the peak locations are unaffected by illumination. Such a finding is important to demonstrate that the proposed chalcogenide glass cladding can be modified once and unaffected by subsequent laser operation producing near- and mid-IR output. Furthermore, these findings demonstrate that the As_2S_3 coating does not degrade over the time of this experiment, an important step to verifying the long term viability of this cladding material.

Figure 6: Comparison of the output spectra of a QCL before and after 5 hours of Illumination at 650 nm. The main peak height remained constant to within error throughout the 5 hour period, but there were some fluctuations in the heights of the secondary features.

5. CONCLUSIONS

The ability for quantum cascade lasers (QCLs) to produce optimized second harmonic generation is limited by the ability to phase match the fundamental and higher harmonic laser propagation in the cavity. In this study, we develop a method of cladding a QCL with a photoactive material whose optical properties can be modified to affect the output of the system and potentially improve the phase matching. The chalcogenide glass arsenic sulfide (As_2S_3) is examined as a potential cladding material. A simple solvent-casting method for the application of As_2S_3 to a QCL is developed and the unimpeded operation of a coated QCL is demonstrated. The material is shown to exhibit the expected increase in refractive index when exposed to above band gap illumination while sub-bandgap illumination results in no change to the index. After illumination for 10 minutes with 312 nm light, the effective index of the laser cavity increases by 9.1×10^{-5} causing a shift in the wavenumber of the mode output of 0.11 cm^{-1} . Further illumination continues to increase the effective index, but at a decreasing rate with a change of 1.3×10^{-4} after 20 minutes. Although additional studies are necessary, these results show for the first time the ability to modify the mode output of a QCL by optically modifying a cladding material.

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