Mid-infrared Al$_x$In$_{1-x}$Sb components for gas sensing

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Abstract. The performance of Al$_x$In$_{1-x}$Sb LEDs have been investigated for a number of aluminum concentrations between 0% and 8.8%. The devices were designed for use in CO$_2$, CO, CH$_4$, NO and NO$_2$ gas sensors since an increasing aluminium concentration produces shorter wavelength LEDs. The sensitivity of the NO gas sensing system was measured and a detection limit of 400ppm was found.

1. Introduction

With tightening legislation on air quality and emissions there is a growing market demand for gas sensors. Many important gases, such as CO and NO, have a strong characteristic absorption in the mid-infrared region ($3-8\mu$m). However, current infrared sensors use incandescent sources and pyroelectric or thermopile detectors which have several disadvantages, including slow response time, limited wavelength range, relatively high power consumption, and a requirement for explosion proof housings to avoid the source igniting other flammable gases which may be present. The replacement of these thermal sources with semiconductor LEDs and the pyroelectric or thermopile detectors with photodiodes would therefore lead to sensors with similar sensitivity but at reduced cost, with real time response, reduced power consumption, and a much wider wavelength sensitivity range.

The overall objective of the research is to develop LEDs and PDs with sufficient brightness and sensitivity to form a viable alternative to the low cost thermal components described above. Our technology is based on the narrow band-gap III-V material Indium Aluminium Antimonide (In$_{(1-x)}$Al$_x$Sb), the band-gap of which can be tuned to provide emission/detection for $\lambda<7\mu$m by varying the aluminium concentration. The devices studied were grown by molecular beam epitaxy (MBE) at QinetiQ Malvern onto semi-insulating 3” GaAs substrates and a schematic diagram of the LED structure is shown in Figure 1.

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LED devices from five wafers were studied, each with a different aluminum percentage as shown in Table 1.

Table 1. Table showing aluminium concentration and gas targeted for the devices tested.

| LED name | Aluminum Concentration | Gas targeted |
|----------|------------------------|--------------|
| LED 1    | 0%                     | NO₂          |
| LED 2    | 2.5%                   | NO           |
| LED 3    | 5.2%                   | CO           |
| LED 4    | 6.1%                   | CO₂          |
| LED 5    | 8.8%                   | CH₄          |

where the active region aluminum concentration was found using x-ray diffraction. In each case the electron barrier layer [1] between the active and the p-type contact regions had an Al composition 15% greater than the remainder of the wafer. The motivation for this work is to develop a suite of high performance devices for use in gas sensing systems for CO₂, CO, CH₄, NO and NO₂ detection and the individual wafers were processed to create LEDs consisting of 16 elements connected in series creating a total emitting area of ~1mm² per LED. This architecture allows the input impedance of the devices to be more easily matched to external circuitry of a gas sensing unit and lowers the sensor noise [2]. After wafer sawing, each LED was mounted substrate down on a TO2 header, resulting in a top emitting device. No antireflection coating was applied and all the measurements were performed at room temperature. The results from a typical device from each wafer are reported along with the predicted sensitivity of the complete gas sensor system.
2. LED Testing

Figure 2 shows the typical forward bias emission spectra, measured on a Fourier-transform infrared (FTIR) spectrometer using a calibrated 77K HgCdTe detector, for each aluminum concentration.

![Figure 2: Measured typical room temperatures emission spectra for LEDs 1-5. The total integrated emittance plotted as a function of Al concentration is shown in the inset.](image)

The devices were driven using a square wave form at 20kHz with a peak current of 100mA (with the exception of LED 5 which was driven at 50mA). The spectra were calibrated using a second calibrated HgCdTe detector, with the devices driven at 1.234kHz square wave, peak current 100mA (with the exception of LED 5 which was driven at 50mA), correcting for the collection efficiency of the optics. Large minima are seen in all the spectra at 4.2µm due to CO₂ absorption. The emittance maxima shifts to shorter wavelengths with increasing aluminum concentration as expected [3], and by varying the increasing aluminum content it is possible to tailor the peak emission wavelength to match the characteristic absorption of a different gas (3.4µm, 4.2µm, 4.6µm, 5.3µm and 5.7µm for CH₄, CO₂, CO, NO and NO₂ respectively). The inset in Figure 2 gives the total integrated emittance as a function of Al concentration. The error in the measurement of integrated emittance was estimated to be ±20%. On all the wafers the variation in emittance for the devices measured was found to be less than or equal to the error in the measurement itself, but for one of the wafers (LED 2) a much larger sample of devices was measured from across the wafer and the error was found...
to be 13%. The LED performance drops as the aluminium concentration increases beyond 2.5%. Work is ongoing to understand the behaviour and to optimise the performance across the whole aluminium concentration range. It is believed that there may be a trap associated with the aluminium incorporation which reduces LED efficiency [4].

3. Measurements of NO concentrations
One of the LEDs, and an associated photodiode (PD) detector, have been used to measure NO concentrations at the Photonic Device R&D Dept of Horiba in Japan. The system used in these experiments is shown schematically in Figure 3.

![Figure 3: Set-up used by Horiba to measure the sensitivity of the gas sensing unit with the NO LED in place. The LED and PD are 95mm apart and the gas cell volume 5.5cm$^3$ and 70mm long.](image)

The LED was driven at 170Hz, 50% duty cycle and 60mA peak current. The photodiode was operated at zero bias. The output signal was measured as the concentration of NO gas was varied from 0% to 4.84%. The system was found to have a detection limit of 400ppm. There is a cross sensitivity issue with water at the NO wavelengths which limits the detection limit. For areas of high water vapour levels a system to reduce them may be required to improve the detection limit. Some applications will have inherently low water vapour levels and so the system could perform sufficiently well as it stands.

4. Conclusions
LEDs have been fabricated to detect a wide range of gases which absorb between 3.4µm – 5.7µm. The emission spectra and total emitted powers were measured for all five LEDs. Excellent total emitted powers have been measured and one LED, for NO detection, has been placed in a gas sensor and the signal versus NO gas concentration measured. The minimum detectable concentration of NO gas was found to be 400ppm which could be improved if water vapour levels were reduced.

Acknowledgements
Horiba acknowledges the support of the Japanese Environment agency (ERCA) for this work. One of the authors (GRN) acknowledges the support of The Royal Society through an Industrial Research Fellowship.
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