ABSTRACT

To achieve net conversion of heat to electricity with thermophotonics, a LED with high external quantum efficiency (EQE) is required. As part of the initial stages of making a thermophotonic device, we have developed a system for accurately measuring the external quantum efficiency of highly radiatively efficient structures. The technique involves measuring uncalibrated photoluminescence and thermal signals from an optically pumped structure, as a function of incident laser power. This allows an increase in fractional luminescence to be calibrated against a decrease in fractional heating. In initial results we have measured an external quantum efficiency of 86% from a GaAs/AlGaAs double heterostructure, with a lower than optimum power density. This is one of the highest EQE values ever reported.

1. INTRODUCTION

1.1 Thermophotonics

Thermophotonics involves the photovoltaic conversion by a receiver cell of radiation from an emitter, which could be heated by various sources including sunlight. A prime difference from normal solar photovoltaics is that emitted energy unable to be used by the receiver can, in principle, be recycled allowing high conversion efficiency. Thermophotonics is a recent development of this concept where the emitter is “active”, namely a heated diode, increasing the rate of energy transfer for a given emitter temperature and concentrating emission in an energy range more suited for conversion by the receiver [1].

A thermophotonic system consists of a heated forward biased light-emitting diode (LED), and an unheated solar cell attached to a load. In order to achieve net conversion of heat to electricity, a very high external quantum efficiency (EQE) LED is required, so that the LED cools when a voltage is applied. The EQE required depends on the applied voltage V via

\[ \text{EQE}_{\text{req}} > \frac{qV}{E_g + kT} \]  

(1)

where q is the electronic charge, \( E_g \) is the bandgap of the LED, k is Boltzmann’s constant and T is the temperature of the LED. As a first step towards this goal, we are aiming to achieve cooling of an optically pumped structure. In this scheme laser light at the bandgap energy \( E_g \) is used to excite electron-hole pairs, which then thermalise with the lattice and recombine, emitting light with energy \( E_g + kT \). Thus the required EQE is \( E_g/(E_g + kT) \approx 98\% \) for GaAs with \( E_g = 1.4\text{eV} \). The EQE required for cooling with optical pumping is generally higher than with electrical pumping. However, cooling should be easier to achieve experimentally with optical pumping, since heavily doped regions and electrical contacts, which introduce parasitic losses, are not needed.

1.2 EQE measurement

Commonly used techniques for measuring photoluminescence EQE involve calibrating the photoluminescence signal with a reflected signal. For samples with EQEs near 100% such methods are not suitable because the difference from unity is a small difference between two large numbers. A way to achieve an accurate measurement of the EQE of such samples is to measure two quantities, which vary with the fractional luminescence, \( \eta_r \), and the fractional heating, \( \eta_r \), respectively. Using this method, uncalibrated measurements of fractional luminescence against a variable such as excitation rate, and uncalibrated measurements of fractional heating against the same variable, are combined to give absolute values of \( \eta_r \) and \( \eta_r \). This method is described in detail by Dunstan [2]. The technique is very general, and the variable could also be, for example, temperature or sample quality. In our case the quantities are the PL signal (\( L_{\text{col}} \)) and the thermal signal (\( \Delta T \)) scaled by the laser power, and measured as a function of laser power. Using these variables, the technique is applicable to samples where \( \eta_r \) varies with the laser power, such as undoped samples where \( \eta_r \) varies with the injection level. Dunstan showed that the calibration factors are uniquely determined by this measurement. That is,

\[ \frac{L_{\text{col}}(P)}{P} = \alpha \eta_r(P); \]

(2)

\[ \frac{\Delta T(P)}{P} = \beta \eta_r(P); \]

(3)

where P is the relative laser power. The optical collection factor, \( \alpha \), and the thermal collection factor, \( \beta \), can be determined by applying the condition

\[ \eta_r(P) + \eta_r(P) = 1 \]

(4)

for all values of P. The EQE is then given by

Note: The text contains mathematical equations and symbols that may not render correctly in some text editors.
where $E_L$ is the laser excitation energy and $E_{PL}$ is the average photoluminescence energy. If $E_L = E_{PL}$, the EQE is equal to the fractional luminescence. For $E_L > E_{PL}$ the excess energy of the laser above the bandgap leads to heating of the semiconductor, due to thermalisation of the carriers, and hence the laser excitation contributes to both the fractional luminescence and the fractional heating. For $E_L < E_{PL}$ the thermalisation of carriers contributes to cooling of the semiconductor. For a sufficiently high radiative efficiency, this leads to net cooling. In this work, aimed at increasing the EQE of the samples and measuring it accurately, laser excitation levels greater than the bandgap are used.

2. METHOD

2.1 Sample preparation and measurement
Thin GaAs/AlGaAs and GaAs/AlGaP double heterostructures were lifted off their GaAs substrates using the epitaxial lift-off technique [3], and mounted on sapphire wafers using van der Waals bonding. For some measurements, a ZnSe dome of 8mm diameter was clamped in place over the sample. The double heterostructures were optically pumped with either a 70mW, 785nm laser diode, or a 500mW, 860nm laser diode, focussed to a spot size of approximately 1mm. A neutral density filter wheel was used to adjust the laser power. The experimental arrangement is shown in figure 1. The laser beam was modulated at 65Hz for the PL measurements and at 1Hz for the thermal measurements. The thermal measurements were performed immediately after the PL measurements at each power level. The modulation was approximately 10% of the steady-state amplitude, in order to keep the injection level (and hence IQE) approximately constant. The PL signal (with an average wavelength of 870nm) was detected with a Si photodetector. The thermal signal was detected with a miniature thermistor. The resistance of the thermistor was measured using a highly sensitive temperature bridge circuit [4]. The temperature bridge circuit uses AC measurements to very accurately determine the resistance of the thermistor.

The signals from the temperature bridge and PL detector were measured using lock-in detection. This allowed very small temperature differences to be measured, regardless of the absolute temperature of the sample. The thermistor was placed on the sapphire wafer, about 3mm from the illuminated spot on the sample, and protected from stray light by reflective tape. Typical signal magnitudes at the thermistor were 30µK, at a measurement frequency of 1Hz. The corresponding temperature variation at the illuminated spot is estimated to be 6mK. The signal drops approximately exponentially with distance, due to the heat capacity and the finite thermal resistance of the sample and sapphire substrate.

The relative power was determined by using a beamsplitter to deflect a small fraction of the laser beam onto a silicon photodetector, and measuring the current from the photodetector.

2.2 Light extraction
Radiative recombination within GaAs is very efficient, and internal quantum efficiencies (IQEs) of 99.7% have been achieved [5]. The main difficulty with achieving high EQEs is extraction of the emitted light, due to the high refractive index of semiconductors (n = 3.5 for GaAs). This means that only light emitted within 16° of the normal can escape from a wafer of GaAs into air, which is 2% of the total radiation emitted within the GaAs. The rest of the radiation is totally internally reflected within the GaAs, and eventually reabsorbed. This is the reason that commercial LEDs generally have efficiencies of less than 2%.

The first step to increasing the EQE is to remove the active layer from the absorbing GaAs substrate. The next step is to alter the geometry of the device to increase the chance of emitted light escaping. There is a range of ways of increasing the extraction efficiency. In this work a dome of ZnSe, a highly transparent, high refractive index material (n = 2.5), has been used. This increases the range of angles that can escape from the GaAs. The dome of ZnSe increases the critical angle to 45°, which is 30% of the emitted radiation. The photons that escape the GaAs strike the surface of the dome at 90°, and hence are transmitted. This approach has been used by Gauck et al. [6], who achieved a 96% EQE with an optically pumped structure, and came very close to achieving cooling.

With high quality material, photon recycling can be a significant factor. When a totally internally reflected photon is re-absorbed by the GaAs, the high IQE of the GaAs means that there is a high probability that a photon will be re-emitted. Since the photon is re-emitted in a random direction, this provides another chance for the photon to fall within the escape cone. However, the resulting EQE is also reduced, via

$$EQE = (IQE)\phi$$

Here $\phi$ is the average photon recycling number i.e. the average number of times a photon is re-incarnated by absorption and re-emission before escaping. The use of a ZnSe dome reduces the value of $\phi$ calculated by ray-
tracing from 37, for a layer in free space, to 4.5. For a sample mounted on a sapphire substrate (n = 1.7) without the ZnSe dome, the value of \( \phi \) is 11. The reduction in the value of \( \phi \) from its value for a sample in free space is due to the escape of light from the edges of the sapphire substrate.

3. RESULTS

The thermal vs. photoluminescence signals, normalised by the relative input power, are plotted in figure 2 for a GaAs/InGaP DH pumped by the 785nm laser diode, without a ZnSe dome. As the input power increases, the normalised temperature signal decreases and the normalised photoluminescence signal increases.

![Fig. 2](image)

**Fig. 2** Temperature vs. photoluminescence, each normalised by the input power.

The results of the calibration are shown in figure 3. The sum of \( L_{\text{ext}}/P \) and \( \Delta T/P \) was constant as expected and the resulting values of \( \alpha \) and \( \beta \) were used to calibrate the luminescence data. The maximum EQE was 60±1% at a power density of approximately 5W/cm\(^2\). This was compared with optical measurements using an integrating sphere, and very close agreement was found [7].

In order to increase the light extraction and injection level a ZnSe dome was applied to a GaAs/AlGaAs structure, and the 860nm laser diode was used. The results are shown in figure 4. The maximum EQE was 86±4% at a power density of approximately 30W/cm\(^2\). This is one of the highest EQEs that have been reported. To the authors’ knowledge, the only higher value is the value of 96% reported by Gauck et.al. [6]. The EQE was still increasing at the maximum power density used, showing that higher EQE values could be obtained with the use of a higher input power density.

This technique can also be used to extract the recombination co-efficients and injection level of a sample, by fitting the EQE data to

\[
\eta_{\text{ext}} = \frac{(B / \phi)n^2}{(2S / d)n + (B / \phi)n^2 + Cn^2},
\]

where \( n \) is the injected carrier density, \( S \) is the interface recombination velocity, \( B \) is the radiative recombination co-efficient, \( C \) is the Auger co-efficient, and \( \phi \) is the average photon recycling number.

![Fig. 3](image)

**Fig. 3** Fractional photoluminescence and fractional heating obtained from the data of figure 2.

![Fig. 4](image)

**Fig. 4** Fractional photoluminescence and fractional heating obtained for a GaAs/AlGaAs DH with ZnSe dome applied.

Using a value for \( B \) of \( 2 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \) [8], and a value for \( \phi \) of 4.5 (calculated by ray-tracing), the injected carrier density and interface recombination velocity can be calculated. The photon recycling number is approximately independent of the internal quantum efficiency for high IQEs. The results of this analysis are presented in figure 5. A value for \( S \) of 40cm/s was obtained. The corresponding internal quantum efficiency is 96.7%, at an injection level of \( 1.2 \times 10^{17} \text{ cm}^{-3} \). At the optimum injection level of \( 8 \times 10^{17} \text{ cm}^{-3} \), the predicted IQE is 99.0% and the predicted EQE is 96%.

In this work the accurate measurement of radiative external quantum efficiency has been applied to optically pumped GaAs double heterostructures. The technique is also suitable for measuring other types of samples with undoped active layers, including LEDs under electrical injection. It is particularly suitable for measuring highly radiatively efficient devices such as thin-film devices on a transparent substrate.

This measurement technique could also be used for GaAs solar cells provided that the EQE varies sufficiently
as a function of injected power; if it does not, another variable such as temperature could be used.

![EQE vs. injected carrier density.](image)

**Fig. 5** EQE vs. injected carrier density.

4. CONCLUSION

In this work we have obtained accurate measurements of EQE by calibrating an increase in photoluminescence against a decreasing in heating, when the signals are normalised by the injected power. For highly radiatively efficient samples, this direct measurement of the fractional heating makes the technique more accurate than techniques that rely on a comparison of the photoluminescence with a reflected signal. EQE values up to 86% have been measured, at a lower than optimal injection level. This is one of the highest EQE values that have been reported.

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REFERENCES