A pplications, Environmental Impact and Microstructure of Light-Emitting Diodes*

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INTRODUCTION
Light-emitting diodes are revolutionising the world of lighting - they are now the light source of choice for everything from bicycle and car lamps to street and traffic lights and giant outdoor video screens.

In this article we provide an overview of the environmental and economic benefits of LEDs and then go on to describe some of our recent studies on the atomic and crystalline microstructure of indium gallium nitride/gallium nitride (InGaN/GaN) quantum-well light emitters using transmission electron microscopy, atomic force microscopy and three-dimensional atom probe microscopy.

APPLICATIONS AND ENVIRONMENTAL ISSUES
Efficiency and energy savings
One reason that LEDs (Figure 1) are more efficient than filament light bulbs is that they stay cool, emitting very little heat. The efficiency of a standard tungsten-filament light bulb is only 5%, so 95% of the electricity supplied to the bulb is lost as heat. Until now, the most economic alternative to filament bulbs has been fluorescent tubes but they are still not highly efficient: a long tube, as used in many offices, is about 25% efficient but the compact fluorescent tubes used in homes are only about 15% efficient. In the UK, 20% of all electricity consumption is for lighting, and in less developed countries, such as Thailand, lighting accounts for as much as 40%.

A US Department of Energy report states that if 50% of the lighting in the USA were replaced by white gallium nitride-based LEDs, 41 gigawatts of electricity would be saved, and so 41 power stations could be closed. Roughly equivalent figures for the UK would be to save eight gigawatts of electricity and close eight power stations (or equivalently not build eight new power stations) that will have to close in the UK) [1]. It has been estimated that white LEDs could save up to 39 terawatt-hours of electricity demand for the UK by 2020 [International Energy Agency (IEA) Report, 2006].

Greenhouse gas emissions
However, the benefits would not just be economic. It is not widely realised that lighting is one of the largest causes of greenhouse gas emissions. The energy consumed to supply lighting throughout the world entails the emission of 1,900 megatonnes of carbon dioxide per year, three times the emission from aviation and 70% of the global emission from cars [IEA, 2006]. It is almost certainly easier to reduce energy consumption and CO2 emissions by using more efficient lighting than it is to produce more efficient cars and aircraft, although doing all three would give maximum benefit. If we can increase the efficiency of lighting to surpass that of tungsten filaments and fluorescent lights then we can save substantial amounts of energy and CO2 emissions.

Applications of coloured LEDs
The first LEDs were red and have been available for about 40 years. They are at least 30% efficient. A typical application is in bicycle rear lights, where in old-fashioned bikes a small tungsten filament light bulb is covered with red glass or red plastic. The efficiency of the light bulb is 5%, and the efficiency of producing red light (through the red glass/plastic) is about 1%. Hence red LED rear bicycle lights are a massive 30 times more efficient than conventional rear lights.

In cars, conventional tungsten filament lights take 0.25 seconds to come on since the electric current has to flow through the filament and heat it white hot (the white light then passes through a piece of red plastic which transmits only the red light). On the other hand, LED brake lights come on virtually instantaneously. If one is driving at, say, 70

Figure 1: A light emitting diode. Courtesy of Olympus Europa.

Figure 2: LED traffic lights.
It has also saved 3,000 tonnes of CO\textsubscript{2} per year in energy, labour and materials costs. To LEDs, saving the City more than $800,000 and green traffic lights have been overwhelmingly over-whelming. Denver, Colorado, was one of the first cities to realise this in the late 1990s. Since then, more than 48,000 of its red, yellow and green traffic lights have been converted to LEDs, saving the City more than $800,000 per year in energy, labour and materials costs. It has also saved 3,000 tonnes of CO\textsubscript{2} emissions per year. All of Singapore and much of China now have LED traffic lights. A public survey in Singapore, after it had totally replaced its traffic lights with LEDs, shows that over 90% of the public preferred the LED traffic signals; better visibility at night, in the rain, and in direct sunlight were the main reasons given. Most cities in the United States are in the process of replacing their existing lights with LED lights, and New York and Las Vegas have already done this. A city can easily save a million dollars a year by replacing all its traffic light bulbs with LED units. In California, the 10% of its LED traffic lights fitted so far have reduced the state’s need for electricity by 10 megawatts, enough electricity to power 10,000 houses. Prominent examples of European cities converting to LED traffic lights include Zurich in Switzerland and Aachen in Germany, with Berlin currently converting. Worldwide, there were 1.6 million LED traffic lights in use in 2002, and this figure will now be substantially higher [1].

**Applications of white LEDs**

White LEDs are already widely used as back-lighting in mobile phones, in flashlights, as interior lighting in aircraft, cars and buses. Audi A6 and A8 cars now use white LEDs as front daytime-running lights, and this year BMW will introduce white LEDs in its top-of-the-range headlamps. White (and coloured) LEDs are increasingly being used to illuminate the outside of buildings. For example, on 23 October 2006, it was announced that the front of Buckingham Palace would be illuminated at sunset every day during the winter, since tourists had complained that they could not see the building after dark. White LEDs were chosen for the illumination because of their low energy consumption, long life and low maintenance.

White LEDs are poised to take over the lighting in our homes and offices, with the substantial energy savings referred to above, but a few more years of research and development are required first. This new form of lighting is so important that the USA, Japan, China and Korea have national research programmes in this field (but sadly not the UK). There are four main requirements for home and office lighting: high efficiency, high quality, long life and low cost. Concerning efficiency, the best white LEDs currently available have an efficiency of 30%, about six times that of filament light bulbs and slightly better than fluorescent tubes. However it must be pointed out that many cheap white LEDs are much less efficient; there are as yet no national nor international standards, so it is a case of ‘buyer beware’. Expert knowledge is required in choosing LEDs. The best white LEDs in the laboratory have an efficiency of 50% and the target for the future is 80%. There seems little doubt that white LEDs will provide a new light source that will be at least 10 times as efficient as filament light bulbs, and at least twice as efficient as fluorescent tubes, with large savings of energy and CO\textsubscript{2}.

The lifetime of LEDs is potentially at least 100,000 hours (about 11 years of continuous operation) but because there are currently no LED standards, it is a case of buy at your own risk. China is planning to use LEDs massively to illuminate buildings inside and out for the 2008 Olympics. However, an eminent Chinese scientist recently told us “LEDs are no good”. When asked why, he said: “The front of many buildings in Beijing have been lit up by LEDs. Now they are all dark, the LEDs are dead.” Our research group has been life testing LEDs, and found that a major problem is poor packaging, and it is for this reason that many will fail after only a few thousand hours. However, we have shown that, with good packaging, the lifetime is at least 100,000 hours. Again, expertise is required in selecting the best LEDs, and manufacturers should be aware that simply reproducing the packaging they have used for red LEDs may not be sufficient for a high quality, white product.

Finally, white LEDs are more expensive than filament light bulbs and fluorescent tubes. For widespread use in our homes and offices, the cost must be reduced. Our group has been funded by the UK’s Engineering and Physical Sciences Research Council and the Department of Trade and Industry, in collaboration with UK industry, to pursue the growth of GaN LEDs on silicon rather than on sapphire, an idea that if successful will reduce the cost of LEDs tenfold.

The near future will see a revolution in lighting. Energy-saving LED traffic signals are with us now and spreading rapidly throughout the world, and they are starting to appear in the UK. In the next five years or so, we should have energy efficient, long life, low-cost lighting in our homes and offices, which will save energy, reduce CO\textsubscript{2} emissions from power stations by 10% and enable us to do (or not do) eight power stations. LED lighting will be the lighting for the 21st century.

**WHAT IS AN LED?**

A light-emitting diode is a chip of semiconductor material doped with impurities to create a p-n junction. Charge-carriers (i.e. negative electrons and positive holes, which can together form neutral electron-hole pairs or excitons) flow into the junction from electrodes with different voltages. When an electron recombines with a hole, it falls into a lower energy level and releases energy in the form of a photon.

The wavelengths of LED emission are a property of the material in which the electron-hole recombination occurs and can vary from the
CRYSTAL DEFECTS IN LEDs

One of the limitations on the performance of LEDs is the presence of crystal defects (dislocations) in the semiconductors which reduce radiative recombination. Indeed, there exists a significant and continuing controversy about the mechanism of light emission in InGaN quantum wells (QWs) which make up the active region of bright blue and green light-emitting diodes, given the high density of threading dislocations (TDs) found in working devices. In all other light-emitting semiconductors, emission is quenched if the dislocation density exceeds about $10^4$ cm$^{-2}$. Yet InGaN quantum wells emit strong blue and green light (depending on the In concentration) when the dislocation density is one million times higher than this value, even though it is known that dislocations in InGaN are non-radiative recombination centers.

ROLE OF INDIUM-RICH CLUSTERS

The limited impact of the high density of threading dislocations in GaN-based LEDs suggests that the charge carriers are in some way prevented from reaching the TDs. This must be due to some aspect of the microstructure of the QW: changes in the QW thickness or composition can provide an energy barrier to the motion of charge carriers. There is clear evidence that, at low temperature, the dominant emission from InGaN/GaN QW structures involves the recombination of strongly localised excitons - i.e. excitons which are trapped at specific sites away from the TDs. This recombination causes this localisation. It has long been recognised that InGaN epilayers could separate into indium-rich and indium-poor phases during prolonged annealing. Thermodynamic calculations show that for typical compositions ($x$=0.1 for blue emission, $x$=0.2 for green) and typical InGaN growth temperatures (600-800°C), the unstrained homogeneous alloy is unstable, leading to decomposition into In-rich and In-poor regions, although it is not clear how applicable these calculations are to the InGaN layers in QW structures. Furthermore, bright-field TEM images of InGaN/GaN quantum well structures have shown variations in local strain along the QW on a ~3 nm length scale. Since an indium atom is much larger than a gallium atom, fluctuations in InGaN compositions will cause variations in lattice parameter, leading to variations in the local strain. By measuring the local lattice fringe spacings using high-resolution TEM lattice images, a two-dimensional lattice parameter map can be plotted, which shows the size of the strain clusters to be typically a few nm. Assuming that this strain is due to compositional variations, the lattice parameter map can be converted to a composition map. For InGaN quantum wells grown with 10-20% indium, the observed strain would indicate an indium content of up to 80%. It is worth noting that the projection problem in TEM makes it difficult to quantify the indium content of these 3D clusters. We call any such clusters 'gross indium-rich clusters'.

However, our recent work on a wide-range of InGaN QW structures has cast doubt on the existence of such gross indium-rich clusters. We observed that InGaN quantum wells damage extremely rapidly in the electron beam of a TEM at the beam currents normally used for imaging. This results in the formation of apparently indium-rich regions which were not present in the original QW. Figure 3 shows (0002) lattice fringe images of an In$_{0.22}$Ga$_{0.78}$N quantum well using high-resolution TEM (HRTEM). The lattice fringe images were obtained with the specimen tilted about 6-7° away from a <11-20> axis towards the adjacent <01-10> pole. At this orientation a systematic row of reflections is excited with (0002) and (000-2) under equal excitation. Figure 4a was recorded within 20 seconds of first exposing this part of the quantum well to the electron beam; Figure 4b is the same area after a few minutes of exposure. We have analysed these images to produce lattice parameter maps. After only a few minutes exposure to the electron beam we found nanometre-size indium clusters had formed which caused local strains of up to 10%, corresponding to an indium fraction $x$ of 60%. These cluster sizes, strains and compositions are typical of those found by others using TEM. However, we have found no evidence at all of gross indium clustering if low electron beam currents are used. At low electron dose, the lattice fringe image of the quantum well and the lattice parameter map are both reasonably uniform (Figure 4).

3D atomic probe studies of indium clustering

Our low-dose TEM studies have revealed that gross indium clustering does not exist in the many InGaN quantum wells we have studied - including samples grown and prepared using a range of different techniques, and commercial samples. However, we cannot rule out lower-level indium clustering as such genuine clustering, if it exists, may be masked by the noise in low-dose TEM images, and genuine clusters cannot be distinguished from indium-rich clusters already created by the electron beam in even low-dose images. So we have used three-dimensional atomic probe (3DAP) microscopy to examine InGaN quantum wells, and assess the homogeneity of the alloy.

Figure 5 shows reconstructions of the InGaN/GaN structure with the indium and gallium atoms displayed. Four indium-containing quantum wells are clearly visible, and we have analysed in detail the indium distribution in the bottom three of these since the top well may have been damaged by sample preparation. We have compared the indium distribution with the expected distribution from a random alloy. No significant deviations were found from that expected in a random alloy for all three of the quantum wells. We therefore conclude that there is no evidence of indium clustering in this sample. Two independent techniques, TEM and 3DAP, have found no evidence for indium clustering in InGaN quantum wells. The 3DAP results indicate that the distribution of In in the InGaN sample studied is that of a random alloy. Local compositional fluctuations must exist, as statistically expected in any random alloy, but there is no observable atomic clustering.

Broad quantum well microstructure

Given that we have shown that InGaN is a random alloy, the mystery of why the high dislocation density does not quench the light emission remains. One option is that there are fluctuations in the quantum well width on a ~3 nm lateral scale, and we are actively research-
ing this possibility. However, it should be noted that whilst localisation at the nanoscale could be important in controlling device performance, the spacing between the dislocations is usually in excess of 100 nm. Hence, the microstructure of the quantum well on a broader scale could also play a significant role in achieving bright luminescence.

We have recently used high-resolution TEM and AFM to reassess the role of the broad-scale QW microstructure in controlling device performance [4]. For background and details of the experimental procedures and methods used see ref 4). Figure 6 shows a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image of the active region of a commercial green-emitting LED. The QWs have gross fluctuations in width. Comparison of LEDs with and without such well-width fluctuations suggests that considerably brighter emission is achieved when the fluctuations are present. In order to understand why this might be, it is necessary to develop a full picture of the 3D morphology of the quantum well, and to understand how the quantum well structure relates to the locations of threading dislocations.

To better understand the morphology corresponding to the well-width fluctuations observed in TEM, InGaN epilayers were studied by AFM. These epilayers were grown using methods (annealing and temperature-bouncing) which are analogous to typical QW growth routes which give rise to gross well-width fluctuations. The AFM images in Figures 7a and 7b show that such epilayers consist of a network of interlinking InGaN strips, about 50-100 nm in width, aligned approximately parallel to the [11-20] direction. In contrast, epilayers which are analogous to QWs of uniform thickness present a terraced morphology.

Figure 8a shows a STEM-HAADF image of a single InGaN strip in an annealed epilayer viewed down the [11-20] zone axis. The numbered crosses indicate the position of the probe for EDX analyses and the In:Ga ratio at each of these points is shown in Figure 8b. These data, and similar electron energy-loss spectra obtained from an annealed QW, suggest that the centres of the InGaN strips are In rich with respect to their edges. Similar studies performed on an unannealed epilayer showed no evidence for varying In concentrations.

Given this compositional non-uniformity, we have postulated that excitons should be confined at the centres of the InGaN strips. However, for high emission efficiency, exciton localisation needs to occur away from non-radiative recombination centres such as TDs. To determine if any relationship exists between the InGaN strips and the position of the TDs, TEM analysis was performed on the annealed epilayer in plan-view orientation. We used a bright-field multibeam imaging technique with the beam orientated along a [1-21-3] zone axis to reveal all types of dislocations; the network structure may be observed simultaneously. Figure 9 shows a series of bright-field images taken down different [1-21-3] zone axes. Each of the images shows the same five TDs projected in different directions with the ends of the TDs that terminate at the network surface indicated by arrows. By comparing the three images, it is apparent that only one TD (circled) terminates at the centre of an annealed QW. However, other TDs terminate at the network while the remaining four TDs terminate in, or very close to, the trenched between the strips. By analysing several areas, we have determined that 90\%±8% of the TDs terminate in the trenched between the interlinking InGaN strips. Thus the overall 3D morphology of the quantum well will lead to a separation between the excitons (which will be localised at the centre of the strips) and the TDs (which tend to lie between the strips). This will prevent the excitons from reaching the TDs and hence reduce non-radiative recombination.

Since we have shown that gross well-width fluctuations are present in commercial LEDs, this mechanism may have broad relevance.

**CONCLUSIONS**

InGaN is used in the active regions of LEDs which are important for the development of environmentally sustainable white lighting. Although many researchers have speculated that light emission from these LEDs relies on the formation of indium-rich clusters in the InGaN QWs, our studies by TEM and 3DAP suggest that InGaN is a random alloy. Hence, other mechanisms for light emission from such QWs must be considered. Here, we have shown that gross-well-width fluctuations may isolate the excitons from the threading dislocations, preventing non-radiative recombination and enabling brilliant light emission.

**REFERENCES**


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