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Further scanning electron microscope studies of GaP electroluminescent diodes

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In green- and yellow-emitting GaP light-emitting diodes (LEDs) both charge collection (CC), i.e. barrier electron voltaic effect current, and cathodoluminescence (CL) signals were recorded as linescan traces across the p–n junctions. A CL dip was observed in every case, corresponding to the CC peak. This effect could be quantitatively interpreted in terms of the competitive origin of the CC and CL signals. The absence of dips from the CL linescan traces of red LEDs can be explained in terms of the saturation of the CL in these diodes at the beam power levels used in the SEM.

1. Introduction

The conductive mode charge collection (CC) current (or EBIC: electron bombardment induced current) arises from the barrier electron voltaic effect [1] at p–n junctions and the variation of this current with x, the distance of the beam impact point from the junction, was shown by Wittry and Kyser [2, 3] to have the form

$$I_{CC}(x) = I_{max} \exp(-x/L) \quad (1)$$

where L is the minority carrier diffusion length. This expression is obtained on the assumption that the beam acts as a source of hole-electron pairs with spherical symmetry such as a point source.

In earlier papers it was reported [4] that linescan traces of conductive mode signals recorded on crossing the p–n junction could be quantitatively interpreted in this way in the case of GaAs [5] but in the case of red-emitting GaP light-emitting diodes (LEDs) this simple theory led to physically unacceptable conclusions [6].

This paper reports the results of further SEM conductive and cathodoluminescent mode studies of GaP LEDs of yellow- and green-emitting types as well as red LEDs. The form of the cathodoluminescence (CL) linescan traces is considered as well as their relation to the CC linescan traces.

2. Experimental techniques

For the CL mode, our SEM is fitted with a liquid nitrogen cold stage and a spectroscopic detection system consisting of an efficient light collecting device, a grating monochromator, a photomultiplier and photon counter circuitry [7].

The diodes examined were all produced at the Allen Clark Research Centre of the Plessey Co Ltd. The green- and yellow-emitting LEDs were produced by growing S-doped, n-type GaP on liquid encapsulated (LEC) Czochralski-grown substrates by a vapour-phase epitaxy process. The epitaxial layer is also nitrogen doped to a density known to result in yellow or green electroluminescence as required. Diffusion of Zn into the epitaxial material was used to produce the p–n junction.

The production of the red-emitting LEDs also started with LEC substrates but both the n-type (Te-doped) and p-type (Zn, O-doped) layers were produced by (separate) liquid epitaxial growth steps.

The CL and CC traces were obtained for SEM linescans across the diode junctions using the same geometry as before [2], i.e. scanning over a face perpendicular to the p–n junction along a line perpendicular to the junction. The CC traces were records of the barrier electron voltaic effect (beve)

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current obtained under approximately short-circuit conditions [3]. The CL traces in the previous work [2, 3] had been records of the "integral CL response", i.e. the uncorrected photomultiplier current obtained with the whole CL spectrum incident on the photocathode. In the present work, however, monochromatic CL signals were recorded from the yellow- and green-emitting LEDs by using the spectroscopic CL detection system. The wavelength chosen for detection was that at the electroluminescent peak for the individual diode. The monochrometer slit width was set to give a modest 5 nm resolution in order to obtain a relatively intense signal to minimize recording times and to make it possible to use relatively short linescan times. In some cases a filter was used to obtain the photon count rate due to the whole CL peak. This will be described as a "semi-panchromatic" CL signal.

3. Results and discussion

3.1. Micrographic and linescan observations on nitrogen-doped GaP diodes

The radiative recombination in green- and yellow-emitting GaP LEDs involves nitrogen. Fig. 1 is a two-part SEM of such a diode. In the upper half the barrier electron voltaic effect current is displayed as video signal while in the lower half the semi-panchromatic CL signal is displayed. It can be seen that, judged both electrically and in terms of CL emission, the junction region is of variable width and position. In this case the electrical junction (upper half of Fig. 1) occurred approximately in the middle of the zone of CL emissive material (lower half of Fig. 1). In other diodes the electrical junction occurred near the edge of the CL emissive zone.

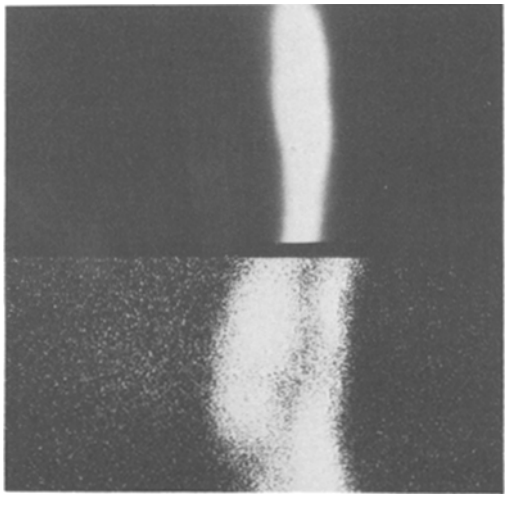

Figure 1 Bipartite SEM of a green-emitting GaP light-emitting diode (LED). In the upper half of the micrograph the charge collection (CC) current is recorded as video signal marking the position of the electrical junction as a white band. In the lower half the semi-panchromatic (green band) cathodoluminescence (CL) signal is recorded as video signal showing the strongly green-emitting, nitrogen-doped region as a broad bright band.

For comparison, Fig. 2 is a bipartite CC and red-peak semi-panchromatic CL micrograph of a red GaP LED. It can be seen that both the electrical junction and the CL-emitting regions are straight and uniform in this case. The CL, like the electroluminescence from these diodes, comes from the p-side of the junction.

A striking feature of the CL micrographs of the green and yellow LEDs, as for example in the lower half of Fig. 1, is the occurrence of a dark band inside the CL emissive zone. This corresponds to the peak of the barrier electron voltaic effect signal as is shown by *Y*-modulation, linescan traces of the conductive and CL mode signals for a single linescan across the junction as in the example of Fig. 3. There is, however, no dark band inside the CL-emitting zone of the red-emitting diodes as can be seen in the lower half of Fig. 2 and there is no dip in the CL linescan traces of such diodes [3].

The same process gives rise to both the barrier electron voltaic effect (beve) peak and the dip in the CL. The beve current arises from the "collection" of holes and electrons by the built-in field to

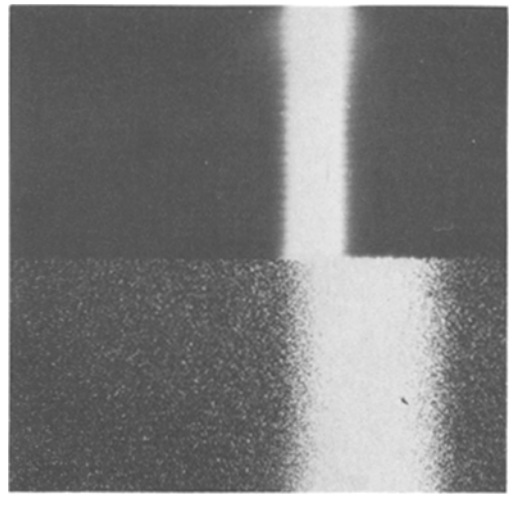

Figure 2 Bipartite SEM of a red-emitting GaP LED. The upper half shows the CC current as video signal and the lower half shows the red-band semi-panchromatic CL signal.

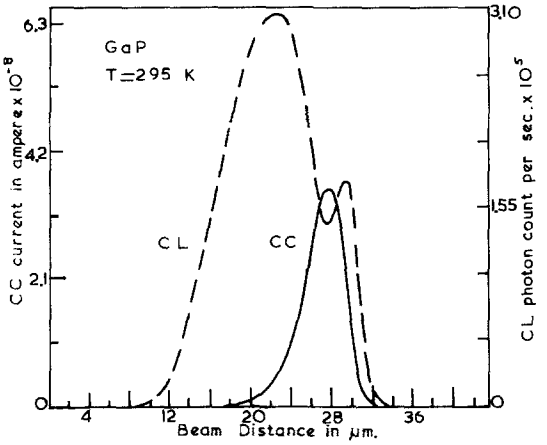

Figure 3 Cathodoluminescence (CL) signal at 570 nm as uncorrected count rate and barrier electron voltaic effect currenct (CC) for a line scan across the p–n junction of a green GaP LED. The CC peak and CL dip occur at the same position and are of similar form.

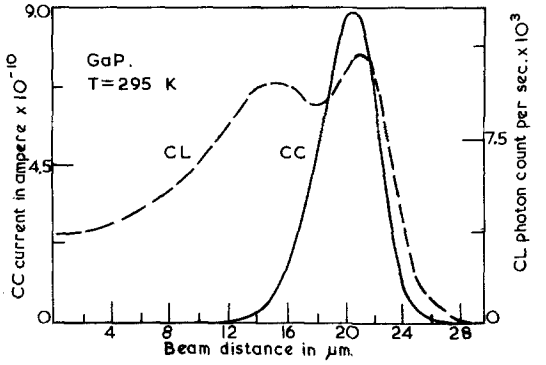

Figure 4 CL (555 nm) and CC linescan traces recorded across the junction of a yellow GaP LED.

that side of the junction where they are of the majority carrier type. They thus cease to be minority carriers on being collected and so cease to contribute to radiative recombination, i.e. to the CL emission. This explanation was put forward in relation to similar CL dips and CC peaks observed in GaAs laser diodes by Wittry and Kyser [3]. This can be expressed algebraically as follows. The CL intensity, i.e. the number of photons emitted per unit time from a point x, $\mathscr{I}_{CL}(x)$, is the product of the external radiative recombination efficiency, η_{rr}, that is the fraction of the excess, injected carriers that combine to produce an emitted photon, times the number of excess carriers $\Delta\eta$. That is

$$\mathscr{I}_{CL}(x) = \eta_{rr}\Delta\eta. \qquad (2)$$

$\Delta\eta$ is the product of the number generated per unit time and the life time, τ. The number of hole-electron pairs generated per unit time by the beam is GI_b/q where G is the generation factor i.e. the number of pairs generated per incident electron, I_b is the beam current and q the charge on the electron. The number of minority carriers lost per unit time due to charge collection is $I_{CC}(x)/q$. Thus

$$\mathscr{I}_{CL}(x) = \eta_{rr}[GI_b - I_{CC}(x)]\tau/q. \qquad (3)$$

If η_{rr} and τ are independent of x, the variation of $\mathscr{I}_{CL}$ with x will be complimentary to that of I_{CC}, the minimum of the $\mathscr{I}_{CL}(x)$ dip should occur at the same point x as the maximum of the $I_{CC}(x)$ peak and throughout the N-doped region $\mathscr{I}_{CL}(x) = \eta_{rr}\tau(GI_b/q) = \text{const}$, producing an intensity plateau in the CL linescan trace except at the junction.

Fig. 3 is an example of traces from a linescan across the junction of a green-emitting LED in which this prediction is satisfied. Fig. 4 is an example of a yellow diode in which the peak and dip are displaced from one another along the line scanned. This discrepancy can be understood in terms of the breakdown of the assumption that η_{rr} and τ are independent of x. The accuracy to which $\mathscr{I}_{CL}(x)$ is constant throughout the linescan plateau depends on the level of development of yellow/green GaP LED technology, i.e. on the control of the doping of the material, and on the quality of the particular diode, i.e. whether any growth- or process-induced defects are present. The sigmoidal (s-shaped) form of the fall from the CL signal plateau will be dealt with later.

The diode of Fig. 4 gave traces that differed from the simple plateau-with-dip form in two respects. The CL dip and the CC peak do not occur at the same position, x, and at the left the CL plateau does not fall to zero but to a large fraction of the peak intensity. These two differences from the simple form were always observed to occur together. When the traces for such a diode were recorded over a sufficient distance, the CL intensity was found finally to fall sigmoidally to zero at some further point.

To test the correspondence in form between the CC peak and the CL dip in simple and in deviant cases the data were replotted as shown for a typical example in Fig. 5, with the CL dip inverted and made equal in height to the CC peak. The correspondence in shape for green- and yellow-emitting LEDs was not markedly different whether the dip and peak coincided in x or not. This

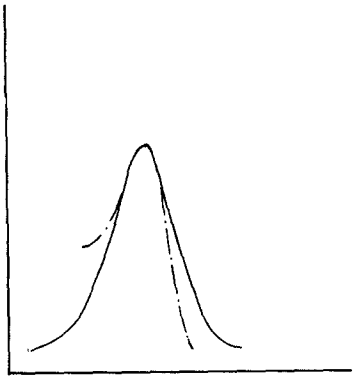

Figure 5 Comparison of the form of the CC peak (solid line) and CL dip (dotted line) for a yellow GaP LED. The CL dip has been inverted and normalized to have the same height as the peak.

correspondence of shape is thus not very strong evidence for the theory.

3.2. CL and CC line scans across red LEDs

The forms of the CL and CC linescan traces recorded for a red GaP LED in the liquid nitrogen stage are shown in Fig. 6. The forms here are similar to those well-known for room-temperature linescans [6, 8, 9]. The CL trace falls sigmoidally from the Zn, O-doped p-side to the n-side. The point at which the CL intensity has fallen to half the p-side value does not coincide with the CC peak. The so-called CL-CC shift [8] between these points was 0.37 μm in the case shown in Fig. 6, and decreased from room temperature to liquid nitrogen temperatures.

It is clear that in this case Equation 3 does not apply since there is no CL dip corresponding to the CC peak. It will be argued later that this is, at least in part, because the CL is saturated in these diodes, so we must write instead that:

$$\mathscr{I}_{CL}(x) = \eta_{rr}(GI_b/q)\tau. \quad (4)$$

The sigmoid form of the CL profile, $\mathscr{I}_{CL}(x)$, can be ascribed to (1) a spatial variation of the radiative recombination efficiency η_{rr} due to the falling concentration of the radiative Zn–O centres, possibly substantially modified by (2) minority carrier diffusion effects, or (3) to the spatial variation of the minority carrier lifetime, $\tau(x)$ or to any combination of these influences.

In view of the simultaneous operation of a multiplicity of factors all of which will tend to produce a sigmoid form of CL trace, the resemblance of these traces to complementary error function plots, i.e. theoretical diffusion profiles, which we found, is of little significance. Indeed it points to the difficulty of extracting reliable data by fitting these curves to the results of detailed calculations relating to the effects of carrier diffusion together with hypothetical concentration profiles as proposed by Van Opdorp [10].

3.3. The form of the CL profile in green and yellow LEDs

In these diodes, the third factor mentioned above, namely the variation of τ with x in Equation 5 was found in these diodes by Blenkinsop *et al.* [11]. If there is fast recombination at the epilayer–

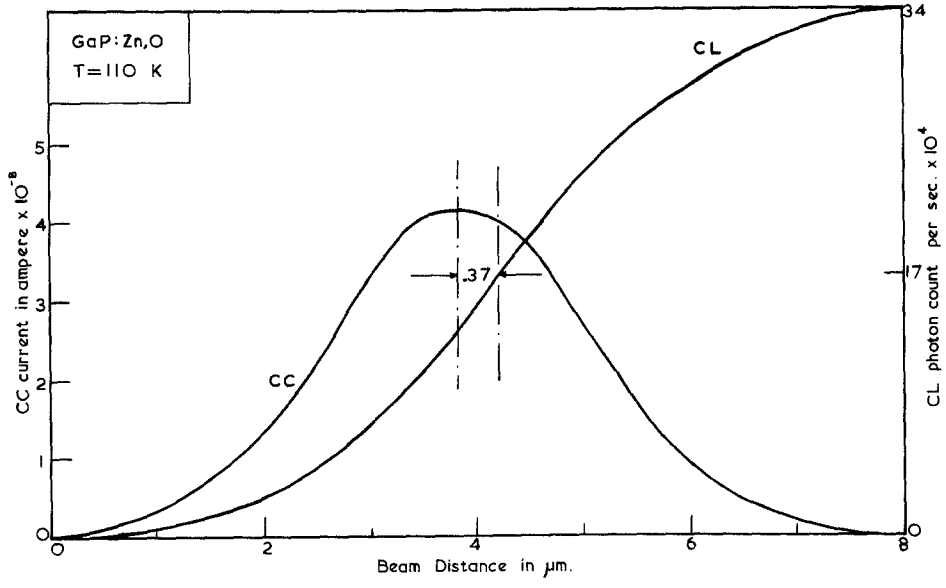

Figure 6 CL (red-emission band) and CC linescan traces recorded across the junction of a red GaP LED held at 110 K.

substrate interface so that the surface recombination velocity $S > 2D_h/x$ where D_h is the hole diffusion coefficient and x is the distance measured from the substrate interface into the luminescent layer, the surface recombination results in a minority carrier lifetime which varies as

$$\tau_s = \frac{x^2}{\pi^2 D_h} \quad (5)$$

near the substrate. The observed lifetime is given by

$$\tau = \left(\frac{1}{\tau_s} + \frac{1}{\tau_b}\right)^{-1} \quad (6)$$

where τ_b is the "bulk" value of the lifetime, assumed to be a constant independent of x.

Substituting Equation 5 into Equation 6 gives

$$\tau = \left(\frac{\pi^2 D_h}{x^2} + \text{const}\right)^{-1}. \quad (7)$$

By direct measurements of τ versus x on diodes of the same type as those studied here, Blenkinsop *et al.* showed that Equation 7 was obeyed in some cases. Clearly Equation 7 is a function which, when substituted into Equation 4, gives a CL curve of sigmoid form, first rising as x^2 then bending over to approach assymptotically the constant bulk (plateau) value of CL intensity.

Our data are not sufficient to enable us to undertake a detailed quantitative test of the alternatives. The CL profiles fall over a distance of about 10 μm (Figs. 3 and 4) whereas the fall in τ in the work of Blenkinsop *et al.* took place over 30 to 50 μm or more, so that the variation of τ is of course, not the only factor determining the form of the sigmoid fall in $\mathscr{S}_{CL}$.

We must next consider the cause of the deviation from the single-stage sigmoid fall to zero CL emission, in some cases. The most likely cause is shown in the CC and CL micrographs of Fig. 7. These show an area of a green LED in which dark diagonal bands intersect the p–n junction which appears as a bright vertical band in the CC micrograph. The direction in which the dark bands run is consistent with the bands being traces of the intersection of {1 1 1} slip bands containing numerous defects with the {1 1 0} cleavage face being scanned. Unfortunately, owing to the small size of the diodes, it was not possible to check this interpretation, for example by etching.

There have been many CL mode SEM studies of GaP showing that individual dislocations appear as dark lines [12–20] and that they reduce the overall lifetime of the material when they are more closely spaced than the diffusion length of the dislocation-free material [13, 16, 17], by acting as non-radiative recombination centres [16] and reducing the minority carrier lifetime locally in long lifetime material [19]. The high dislocation density could also be responsible for the marked non-coincidence of the CL dip and CC peak in these linescans.

3.4. The effect of beam voltage on the form of the CC peak in red LEDs

For red GaP LEDs when the log of the barrier electron voltaic effect current log I_{CC}, was plotted

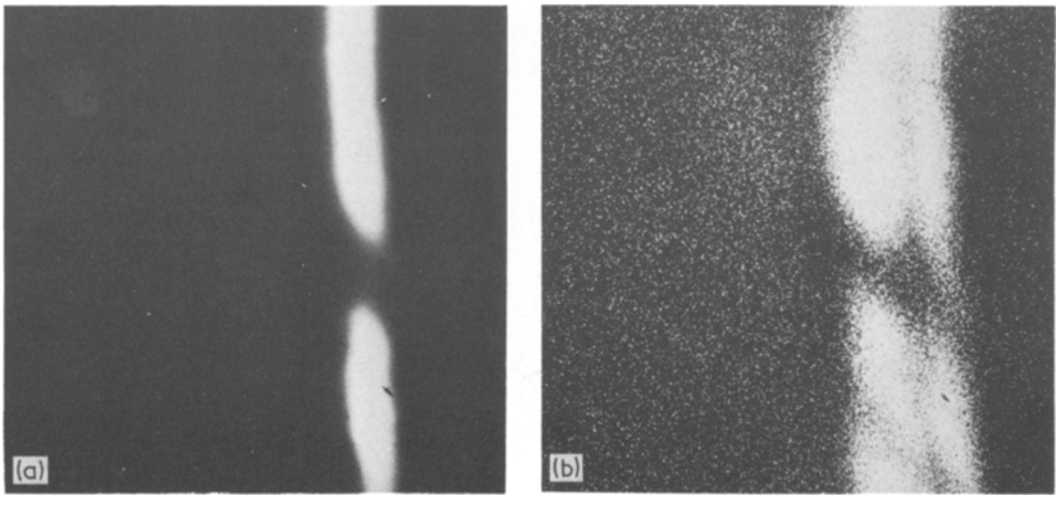

Figure 7 (a) CC and (b) CL (565 nm) SEMs of a green-emitting GaP LED.

against x, the straight lines obtained changed slope with changing electron beam voltage V_b [3, 9]. On the assumption of a point or uniform spherical volume generation of carriers, i.e. of Equation 1, these observations imply that L is a function of the beam voltage which is not physically acceptable. By taking account of the finite size of the electron beam and of the form of the current distribution over the beam diameter, Lengyel obtained plots with the property that the slope of the log of I_{CC} versus x, varies with a parameter proportional to the beam radius [21]. Experiments carried out in the course of the present work showed that under the experimental conditions used previously [6], i.e. that the beam power $E_0 = V_b I_b$ was kept constant as V_b was varied, the beam radius varied linearly with V_b [22]. Moreover, as pointed out by Davidson [23], the point source or uniform generation throughout a spherical volume approximation is quite inappropriate at high beam voltages as used here. A better approximation is that the energy dissipation per unit volume, which controls the carrier generation rate, falls off exponentially with distance from the point of impact of the beam. The charge collection current would therefore tend to vary exponentially with x due to this exponential variation of the generation rate from the beam impact point with the beam voltage. Thus the observation of beam-voltage dependent slopes in $\log I_{CC}$ versus x plots is accounted for by non-spherically symmetrical carrier generation effects.

4. Discussion

The inverse relation between CL intensity and CC current of Equation 3 applied in the cases of the green and yellow LEDs, but not in the case of the red LEDs. This can readily be accounted for, if the CL is saturated in the red LEDs but not in the yellow and green LEDs. Let the density of hole-electron pairs injected by the beam be Δn_0. Assuming that these are uniformly distributed throughout a "cascade" volume V

$$\Delta n_0 = \tau G I_b / qV. \tag{8}$$

The reduction in that density due to charge collection by the barrier electron voltaic effect results in a density given by

$$\Delta n_1 = \tau(GI_b - I_{CC})/qV. \tag{9}$$

Suppose that Δn_0 and Δn_1 fall in the fully saturated range of densities so both densities give rise to the same CL intensity, then no reduction in CL signal will occur in the region of the CC peak and Equation 4 rather than Equation 3 applies, as is observed to be the case for red LEDs.

On the other hand, suppose that in the range of the injected and reduced pair densities, Δn_0 and Δn_1 the CL is not saturated but varying approximately linearly with excitation, then the CL intensity will be reduced in proportion to the density reduction, $I_{CC}(x)/qV$. In such a case, Equation 4 will apply. Fig. 4 is thus evidence for approximately linear CL excitation (η_{rr} constant) in this work.

There is both experimental and theoretical evidence to support the assumptions of CL saturation in the case of the red LEDs but not that of the green and yellow LEDs. It was noticed at the beginning of this work that satisfactory CL intensities were obtained from the red LEDs for any beam current, voltage and diameter conditions that were normally employed, but that when green and yellow diodes were examined, adequate CL intensities were obtained only for the highest attainable beam powers. In fact, deterioration of the green and yellow LEDs under these bombardment conditions was so rapid that protracted and repeated measurements on a single diode were not possible. Attempts were made to measure CL signal strengths as a function of injection densities. The results were in line with the idea that the red LEDs were saturated, but the experimental errors were large and the irreproducibilities marked. These experimental limitations arose essentially from the fact that our existing large Faraday cage for beam current and diameter measurements cannot be used simultaneously with the semi-ellipsoidal mirror, etc, of the CL detection system, which fits closely round the specimen.

The materials parameters of the red-, green- and yellow-emitting LED materials make it likely that the CL is saturated in the red case only. The red material was doped to a level of only $10^{16}\,cm^{-3}$ or less of O to form the Zn, O acceptor–donor recombination centres, and the effective lifetime for decay in this case was $\tau \simeq 300$ nsec, whereas the green and yellow material was heavily doped ($\sim 10^{19}\,cm^{-3}$) with nitrogen recombination centres, and gave fast recombination $\tau \simeq 20$ to 30 nsec, (G. Lidgard, Allen Clark Research Centre, the Plessey Co, private communication). The long lifetime in the red material implies large injected densities (Equation 8) in relation to the low density of

recombination centres, while the nitrogen-doped material had lower injection densities because of the order of magnitude lower value of τ and three orders of magnitude higher radiative recombination centre density. Saturation of the centres with trapped carriers is thus far more likely in the Zn, O-doped (red LED) material than in the N-doped (green and yellow LED) material, in accordance with the hypothesis put forward above.

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