# The influence of water and ethanol adsorption on the optical blinking in InGaN quantum wells

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**Abstract.** We studied the adsorption of liquids over the surface of InGaN quantum well based wide band-gap devices and found that the immersion in certain liquids has noticeable effects on the optical blinking phenomena. We used two samples with different indium concentrations, emitting on the green and blue range, and immersed them while under direct illumination with 365 nm UV light. We found that especially water and ethanol provoked evident optical variations compared to observation in air. While blinking spots can be observed irrespective of the In concentration, their contrast and luminosity increased for samples with the emission in the 510 nm range, rather than for those in the 460 nm. Based on these results, we put forward the hypothesis that the presence of liquids induces the formation of radiative centers, possibly complexes related to intrinsic defects binding with adsorbed impurities, such hydrogen or oxygen.

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## 1. Introduction

Due to the progress in GaN growth and device manufacture, light emitting diodes (LED) are currently employed for a variety of applications, like visible light communication or traffic lights. Despite the importance of GaN-based LED, the correct functionality of such devices is still undermined by a variety of issues, e.g., high density of defect states or large strain-induced polarization caused by lattice mismatch. In particular, the optical blinking phenomenon and the optical memory effects[1, 2] affect the optical quantum efficiency of InGaN single quantum wells (QW).

The blinking phenomenon (blinking in short) is observed not only in InGaN QW, but also in many crystals such as CdSe nanocrystals[3] and GaAs quantum dots (QD)[4], where the emission intensity becomes unstable. In InGaN, blinking is induced by illuminating the surface of the sample with a 365 nm light that excites not only the InGaN layer, but also the GaN layer. Blinking is known to occur in localized domains where the optical emission is more intense than the average, called intense luminous centers (ILCs)[1]. While blinking always occurs in ILCs, not all of them are blinking. As a matter of fact, most ILCs show only stronger optical intensity, which is caused by accumulation of carriers in localized regions with high In content[5, 6, 7, 8]. Based on this, a correlation between such spatial nonuniformity of In composition and blinking was also put forward[9]. This effect was confirmed in several studies, mainly in samples with emission peaks of 510 nm and 540 nm. For samples that emit blue light such as 460 nm, the same optical blinking can be observed, but it is less prominent and noticeable[1, 8].

Among the possible causes of blinking in an InGaN QW, the quantum confined Stark effect is one candidate[1, 10, 11]. However, this cannot explain the experimentally observed intensity distribution of the blinking[1, 12]. Later, it was proposed that the interference of thermal vibration of the crystal lattice may be the cause of the unstable blinking[13]. However, this idea considers local phenomena and does not concern the external species present on the sample surface. In a recent study, Tsutsumi et al. found that the concentration of ILCs increased when oxygen is adsorbed on the surface of an InGaN QW[14], suggesting that blinking could be caused by the interaction of surface molecules with impurities present within the QW.

By considering the above hypotheses, we decided to verify whether or not blinking is caused by the interaction between species adhering to the surface and intrinsic impurities. In order to do this, we present a detailed study on the effects of liquid adsorption, mainly water and ethanol, on the total luminosity and presence of ILCs in two InGaN single QW devices with emission peaks of 460 nm and 510 nm.

### 2. Experimental Details

The samples used in this experiment are a stack of undoped GaN layer (4  $\mu$ m) with a thin In<sub>x</sub>GaN<sub>(1-x)</sub> active layer (3 nm) capped by an undoped GaN layer (5 nm). The sample is grown in the (0001) direction by metal-organic vapor phase epitaxy (MOVPE) on sapphire.

The emission peaks of the samples depend on the In concentration x in the layer, this can range between 400 nm up to 540 nm or over[5]. For the current study we employed two samples, one emitting at 460 nm the other at 510 nm.

Prior to optical observation, samples underwent one minute in ultrasound sonic bath (US-2R, AS ONE, Japan) in distilled water. The samples were inserted in a custom made cell and fully immersed in different liquids, then photoluminescence (PL) measurements were performed by attaching a CCD camera (HDR-SR1, SONY) to a selective excitation fluorescence microscope (BX51WX, Olympus). The optical emission from the surface was recorded at 30 frames per seconds and stored in AVI format. We grouped our recordings in 30 s chunks for analysis (the short initial lamp induced transients were cut away). Ultraviolet Hg lamps were used as excitation light (365 nm and 405 nm emission lines), the thickness of the liquid layer was 500  $\mu m$ , the absorption spectra of water and ethanol in those two UV ranges is nearly identical[15]. Since the main purpose of the investigation was to detect the ILCs changes caused by the presence of liquids, all our observations were made using the sole 365 nm excitation light that excites both the InGaN layer and the GaN layer[1].



**Figure 1.** The photoluminescence of the sample in air and fully immersed in liquid at two emission wavelength. The photoluminescence maps are in panels (a), (b) and (c) for the sample emitting at 460 nm, in air, water and ethanol respectively. In panels (e), (f) and (g) again air, water and ethanol for the other sample emitting at 510 nm. It can be seen that the bright spots (ILCs) are increased due to the adhesion of the liquid in spite of the fact that temperature, optical excitation, location and any other physical parameters are identical. All the samples are excited by a UV light of 365 nm. All images have the same scale of panel (a).

#### 3. Results and Discussion

Once fully immersed in a liquid, different optical fluorescent patterns and an enhanced blinking dynamics were detected. To verify this effects, tests were carried out using several liquids. We found that water and ethanol are the two liquids that visibly alter the optical InGaN

emission pattern and remarkably increase the number of blinking points in a reproducible manner, please see the videoclips in the supplementary media (they show 30 seconds of recording for the 510 nm samples in air and ethanol).

Fig. 1 is a comparison of the sample surface before and after the immersion in liquid. Although the area had in air few ILCs (panels a and e), their number increased noticeably in presence of water (b and f) and ethanol (c and g), while the blinking became distinctly more intense after ethanol. In addition, while the number of ILC increased, there were regions where the light emission was weakened by the presence of the liquids and become darker, improving the overall contrast.

As the figure shows, since the number of ILCs increased in the presence of liquids and since they occur in regions of high In content[1, 5, 6, 7, 8], our results suggest that the adhesion of the liquid to the sample surface facilitates the collection of carriers in such In-rich regions, where radiative carrier recombination occurs with higher rate. More specifically, the fact that carriers are localized in In-rich regions[6, 16] suggests that the liquids might introduce impurities that lead to the formation of highly localized radiative centers.

Concerning those domains that look darkened in presence of liquids, we can hypothesize that the missing carriers migrated to those ILCs that have become more intense. This is consistent with previous studies reporting movement of carriers from low optical emission regions to higher optical emission regions[5] and longer lifetime localized areas[6].

In fig. 2, we map the time-wise standard deviation of the optical emission intensity in the same regions of fig. 1. This was done in order to quantitatively demonstrate that the ILCs are actually changing intensity in time (blinking). The standard deviation was calculated pixel-by-pixel, analyzing 30 s of data, for the sample in air ((a) and (b)), water ((c) and (d)) and ethanol ((e) and (f)). In short, the map represents the optical variability of each pixel. The wider the intensity distribution of the blinking points, the larger the standard deviation. In these maps absence of blinking, despite the higher intensity, results in a lower standard deviation.

Fig. 3 represents the distribution of the standard deviation's histogram cumulative frequency integrated along all the sample surface for each sample in air, water and ethanol, for emission at 460 nm (fig.3a) and 510 nm (fig.3b). Although the histograms might appear similar for each condition, by looking at the steep rise of the cumulative curve, the effect of liquid adhesion is apparent. In fact, when the samples are fully immersed in water or ethanol, the curve rises slower. We have to keep in mind that the horizontal axis represents the optical intensity fluctuations (standard deviation) and, since a higher standard deviation indicates stronger blinking, a slower growth of the cumulative value signifies a spread of the histogram toward higher values of standard deviation, that is intense blinking. As it can be understood, the cumulative histogram is a way to make some of the features of the histogram more evident. In our case, it exposes the higher blinking in a consistent way, better suitable than the bare histogram plot where the three standard deviation histograms (for air, water and ethanol) overlap and their differences are difficult to grasp.

To have a quantitative insight into this effect, we fitted the cumulative frequency with a

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**Figure 2.** Standard deviation map of samples in (a) and (b) air, (c) and (d) water, (e) and (f) ethanol, for 460 nm ((a), (c), (e)) and 510 nm ((b), (d), (f)) emissions. The blinking points appear to increase in number and variability due to the adhesion of the liquid (note the color scale differences). Two ILC, labeled A and B, will be discussed later in the text. All images have the same scale of panel (b).

Boltzmann sigmoid

$$f = f_{\infty} + \frac{f_0 - f_{\infty}}{1 + e^{(x - x_0)/\tau}}$$
(1)

where  $x_0$  is the center of the sigmoid,  $f_0$  and  $f_{\infty}$  are the initial and final value of it and  $\tau$  represents its slope inclination. Plotting  $\tau$  for the three conditions studied (air, water and ethanol), the effect of the liquids is clearly noticeable as shown in fig. 4.

Since the blinking points are located at ILCs in In-rich areas[1, 5, 6, 7, 8], their distribution, in the standard deviation map of fig. 2, reflects the spatial distribution of the In composition in the sample. Even if the presence of the liquids enhances the standard deviation in these local domains, it is difficult to detect blinking averaging the optical standard deviation on all the surface of the sample, because this means averaging the local indium fluctuations. In fact, the average standard deviation calculated on all the surface, for each sample, is approximately 2 (a.u.), whereas in confined regions of the maps of fig. 2, blinking points shows standard deviations of 10 or more, that is 5 times or higher. This averaging explains the reason why previous large scale studies on InGaN did not show fluctuations or blinking[1].

With our methodology we could compare individual ILCs optical emission profile for



**Figure 3.** Histogram of the standard deviation maps in figure 2. Panel (a) represents the 460 nm sample and (b) the 510 nm one. The horizontal axis is the standard deviation. The histogram is clipped up to the range where their cumulative relative frequencies approach approximately to 1. The cumulative line plots indicate that the standard deviation, that represents the optical blinking, is increasing due to the presence of water and ethanol, with ethanol showing consistently a stronger effects on both samples.

each condition. Figure 5 shows the change in the intensity of the emission of two ILC (those indicated by the arrow in fig. 2). The three plots show the photoluminescence in the same local area for each of them. The blue-emitting 460 nm (ILC A) in ethanol shows less prominent variations when immersed in different liquids compared to the 510 nm ILC B (notice the scale that is higher for the greener sample). In contrast, when immersed in water or ethanol, ILC B shows an intensity much higher than prior to the immersion. Since the 460nm sample has less Indium than 510nm, these results further suggest that In concentration favors optical emission following adsorption of liquids compared to PL in air and, at the same time, it promotes blinking in same areas. Moreover, although blinking was previously thought to have an adverse effect on light emission, this experiment shows that liquid adsorption has a strong effect in the confined region of ILC, but improves or does not alter much the total PL emission averaged on all the surface of the sample. In addition, since it is considered that the ILC emit light by concentrating a large number of carriers in a confined region, our results suggest that the blinking in the InGaN QW depends not only on the presence of In-rich regions, but might



**Figure 4.** The slope  $\tau$  of the cumulative frequencies of the distributions in figure 3 when fitted with equation 1. The increased  $\tau$  resulting when immersed is noticeable on both samples. All the  $\tau$  shown and error bars are the result of a fit with  $R^2$  better than 0.99.

also be affected by the presence of impurities (like H, C, O), due to adsorption of liquids, very near the quantum well (the capping layer of the samples is few nm, so the liquids are in proximity to the QW).

To this end, it can be speculated that the detection of these ILCs, in such In-rich regions, might be linked to the formation of radiative centers involving intrinsic defects. As a matter of fact, In-rich regions are typically associated to low crystalline quality[17], due to the presence of V-shaped defects formed by dislocations gliding to the surface[18]. The interaction between impurities and dislocations was studied theoretically by Jones et al.[19] and it was concluded that the formation of complex defects is possible. For this reason, since a high density of dislocations means that the concentration of gallium vacancy ( $V_{Ga}$ ) and nitrogen vacancy ( $V_N$ ) is high, we can put forward the hypothesis that, in such In-rich regions, complex defects with either oxygen or with the addition of hydrogen can form. As a matter of fact, a rather high density of  $V_{Ga}$  can be expected in GaN grown on sapphire[20], like the samples analyzed in this study. In addition, H and O are rather common impurities found in metal-organic chemical vapor deposition (MOCVD) grown materials and they are energetically favorable at empty N-sites[21]. In particular, O can be adsorbed at GaN surfaces[22, 23, 24]. By considering these factors combined, it can be speculated that the adsorbed O might diffuse along the dislocation[25], where it can give rise to  $V_{Ga}$  related complexes[26], e.g.  $V_{Ga}$ -O<sub>N</sub> is known to be a source of green luminescence[27]) and is thermally stable up to 1500 K[28].

It can be argued that O diffusion might be difficult to occur at the temperatures employed in this study (RT). However, Pearton et al. have shown that, after growing SiO<sub>2</sub> on GaN at 50  $^{o}$ C, a significant concentration of O could be detected in GaN up to a depth of 40 nm. Since dislocations provide an energetically favorable path for its diffusion[25], with an activation energy that can be half of that required in the bulk[25], it is not unreasonable to hypothesize the diffu-

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sion of O occurring even at RT. We point out that, according to theoretical calculations, H can also be adsorbed on GaN surfaces[29], so the involvement of H in such radiative centers might not be ruled out. It is also worthwhile noting that radiative complexes might form throughout the InGaN QW, but the lower the In concentration, the lower their density. In addition, a lower In concentration results in deeper electrically active levels in the band gap for the same defect[30], thus altering the optical emission properties of such radiative complex. As a possible follow-up to the present study, positron annihilation spectroscopy (PAS) or electron paramagnetic resonance (EPR) might be carried out, in order to verify the presence of these  $V_{Ga}$ -related complexes in our samples.



**Figure 5.** The time profile of the photoluminescence emission of the ILC A (panel (a)) and B (panel (b)) indicated in figure 2 in the three conditions air, water and ethanol. In both regions, but especially for the ILC B that is located on the 510nm emitting sample, the intensity is increased locally and its variability, the blinking phenomenon, is also evidently enhanced by the liquids.

Table 1 shows the average value of the overall intensity of the samples, in air or immersed in the liquid. As it can be seen, the overall strength was basically smaller in liquid. However, when water was introduced on the 510 nm sample surface, the overall emission intensity

	Air	Water	Ethanol
460nm	111	98.8	101
510nm	68.0	81.5	68.0

**Table 1.** Comparison of overall average strength of each sample in presence of liquids. Clearly their overall effect on the average intensity is much smaller than the confined effect on local emitting domains.

increased. Since this is a change in intensity of about 20% compared to the sample in air and is locally dis-homogeneous, this variation is considered not useful for industrial applications. However, since there is the possibility that the covering model discussed by Tsutsumi et al.[14] can be applied to the current experiment to model the relationship between the surface state due to liquid adhesion and the emission intensity changes, we plan to investigate the overall emission variations occurring during the evaporation of the liquid.

#### 4. Conclusions

We exposed InGaN single quantum well samples, with emission wavelengths centered on 460 nm and 510 nm, to water and ethanol, at room temperature and performed photoluminescence measurements with excitation light of 365 nm. As a result, we confirmed that the bright spots and blinking domains normally present on these samples in air, increased in both cases. The facts that the emission intensity can be linked to the presence of In-rich regions and that blinking requires also a large number of carriers, suggests that such intense luminous centers might be due to the presence of V<sub>Ga</sub>-related defects, possibly bound to oxygen donors. We believe that the method of creating an optical variability standard deviation map and examining its spatial structure reveals novel information about the sample internal carrier dynamics. Moreover, the histogram analysis has been proven to be useful for the understanding of the effect of liquid absorption on the local optical dynamics.

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