The relation between photoluminescence properties and gas pressure with [0001] InGaN single quantum well systems.

Toshiaki Tsutsumi

Department of Nanosystem Sciences, Yokohama City University, Yokohama 236-0027, Japan

Giovanni Alfieri

Department of Electronic Science and Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo, Kyoto 615-8510, Japan

Now at ABB Corporate Research Center, Switzerland

Yoichi Kawakami

Department of Electronic Science and Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo, Kyoto 615-8510, Japan

Ruggero Micheletto

Department of Nanosystem Sciences, Yokohama City University, Yokohama 236-0027, Japan

Now at Harvard Medical School, Cambridge, 02139 MA, USA

Abstract

We show for the first time that photoluminescence of InGaN single quantum wells (SQW) devices is related to the gas pressure in which the sample is immersed, also we give a model of the phenomena to suggest a possible cause. Our model shows a direct relation between experimental behavior and molecular coverage dynamics. This strongly suggests that the driving force of photoluminescence decrease is oxygen covering the surface of the device with a time dynamics that depends on the gas pressure. This aims to contribute to the understanding of the physical mechanism of the so called optical memory effect and blinking phenomenon observed in these devices.

Keywords: Science, Publication, Complicated

1. Introduction

InGaN-based LED of green-ultraviolet region and white LED with phosphor have come into practical use. However, the crystal growth methods and understanding of InGaN devices are still affected by the lack of knowledge about the theoretical background on different phenomena{1}. For instance, despite the large concentration of threading dislocations ($10^8 - 10^{10}\ cm^{-2}$){2, 3} due to lattice mismatch{4}, InGaN optical devices achieve very high internal quantum efficiency and optical emission. In addition, InGaN quantum wells with high Indium composition domains, such as quantum dots (QDs), are known to induce local excitation emission (bright spots/points){5}{6}. Recently, instability blinking{7, 8} and optical memory effect{9}], observed by PL in InGaN Single Quantum Well (SQW), were reported and associated to the presence of defects and strain within the crystal{10}. Instability blinking was found in CdSe nanocrystal{11, 12} and epitaxial grown film{13, 14}, ZnCdSe quantum dots {15, 16}, GaAs QD{17, 18}, InP QD{19, 20, 21} and Porous silicon. In InGaN SQW, instability blinking arises around a QD in a region of few μm of diameter and the flashing intensity width is temperature dependent{22}. Therefore, the phenomenon was associated to beating of slightly different thermal wave vibration creating unstable optical blinking{23}. Optical memory effect in InGaN is the phenomenon in which photo-luminescence emission becomes gradually stronger on a time scale of seconds to few minutes and depends from the previous illumination history of the sample{9, 24}. A complete and universally accepted theory to explain these two phenomena is not available.

2. Methods and results

In this study, we employed InGaN SQW grown in (0001) direction with the MOVPE method (fig. 4). The InGaN SQW layers are composed of an undoped GaN layer (4 μm) on a sapphire substrate, an InGaN active layer (3nm), and an undoped GaN layer (5nm). The main peak of the bulk macroscopic photo-luminescence was about 540nm, see figure 4 taken in near field optics conditions (Micheletto et al. {5}). The SQW was optically characterized by the experimental setup shown in Fig. 2. The sample in placed in a vacuum chamber (RC102-CFM, CIA, Inc.), connected to a turbo-molecular

vacuum pump (TSH 071 E, Pfeiffer), to a temperature controller (Model 32, Cryogenic Control Systems, Inc.) and a gas cylinder. The dynamics of the photo-luminescence is detected by using a selective excitation fluorescence microscope (BX51WX, Olympus) coupled with a CCD camera (HDR-SR1, SONY). The time variation of the light emission surface is recorded as video data at 60 frames/second. Ultraviolet Hg lamp was used as excitation light (365nm and 405nm emission lines). The 365nm light excites both of InGaN layer and GaN layers. On the other hand, 405nm light excites only the InGaN layer.

In Fig. 4, we show the effects of air pressure (from 1000 mbar down to 1.0×10^{-5}mbar) on the photoluminescence, when the sample is excited at 365nm. It can be seen that the overall emission intensity changes according to the degree of vacuum. The gray curve represents the change of pressure in log scale, whereas the dots are the sample luminosity, averaged over the entire surface. The sample is excited by a 365 nm line. We see that whole emission intensity varies dynamically depending on pressure. In high vacuum, the emission improves and grows to a plateau 40% higher than the baseline at one atmosphere. Also, the luminosity distribution becomes homogeneous as blinking points and intense luminous centers{5} seem to disappear. On the contrary, at air pressure, the intensity drops to lower values and the emission spatial distribution is less uniform with many bright points, some of those result to be blinking, see the insets in figure 4 for two pictures taken at the beginning and the end of the experiment. These images are taken exactly on the same spot and the variation of appearance of the luminescence is striking. See also the optical emission of the sample, taken in near field optics conditions and centered on one of the intense luminous center (figure 4)

On the other hand, exciting the sample at 405nm we observe small changes of intensity in response to pressure, the PL emission on the surface is homogeneous and we do not observe blinking points (figure 5). Since with 405 nm we do not excite the InGaN layer, this suggests that the blinking and those Intense Luminous Centers are associated with the GaN/InGaN interface in proximity of the surface.

To understand the physical mechanism that drives this effect we have to consider that, in general, adsorption by Van der Waals' forces on the surface of a material changes with the degree of vacuum. The presence of blinking points and overall emission intensity depends on pressure, suggesting that

the phenomenon is driven by a change in the amount of adsorbed species on the surface. In order to prove this, we proceeded by creating vacuum in a room temperature chamber (about 300 K and 1×10^{-5} mbar) and then by injecting gases, like air, pure dry air ($O_2 : N_2 = 2 : 8$), N_2 gas, Ar gas, and CO_2 into the chamber, reaching up to a pressure of 1000 mbar (1 atm). Following the injection of each gas, we observed the variation of PL emission. Since there are almost no optical emission variations when InGaN SQW is excited with 405nm wavelength, in the following experiments we used 365nm excitation light only. In Fig. 6 it is shown the PL profile when a sample excited by 365nm wavelength is brought back from high vacuum condition to 1000 mbar for each injected gas. It can be seen that air and pure dry air greatly reduce the PL emission. On the other hand, Ar and CO_2 gas have a low impact, whereas N_2 gas have an intermediate effect. Based on this evidence, we put forward the hypothesis that molecular oxygen is the most effective specie and the main cause of emission variation. This is in accordance with what reported by both Zywietz et al {25}, who showed that GaN surface is very active towards oxygen incorporation, and by Pearton et al. {26}, who experimentally demonstrated that oxygen can be found in GaN up to a depth of 180 nm. More recently, density functional theory calculations revealed that oxygen can be easily incorporated into InGaN mono-layer QW (MLQW) {27} in accordance with the experimental results of Kappers et al. {28} who reported that growing N-poor InGaN leads to high levels of oxygen incorporation. The detrimental effects of oxygen in InGaN are known: it can compensate dopants, making the growth of p-type InGaN difficult{29} and it has been held responsible for the degradation of InGaN/GaN LED{30, 31, 32}.

3. A model for the photo-luminescence dynamics

We model the relation between emission intensity and ambient pressure in order to give an explanation for the decreased emission at higher pressure. We base ourselves on a simple molecular coverage dynamics theory. We suppose that the optical emission, generated at the InGan/GaN interface, is decreased by the presence of absorbed molecules on the surface accordingly to this linear relation:

$$I(t) = -n(t)\beta + I_{max} \tag{1}$$

where $n(t)$ is the number of molecules present on the surface at time t, β is the loss of luminosity for each molecule and I_{max} an offset. The term

I_{max} represents the maximum luminosity the sample can have if there are no molecules on the surface.

To model how $n(t)$ varies in time, we consider a space where molecules can be absorbed or desorbed as an uni-dimensional line representing the surface of the sample. For simplicity hereafter we call it "surface" and the rate of change of n can be expressed as follows:

$$\frac{dn(t)}{dt} = -n(t)\gamma_{des}(t) + (n_{max} - n(t))\gamma_{abs}(t) \tag{2}$$

the first term $-n(t)\gamma_{des}(t)$ represents the molecules that leave the surface per unity of time. The parameter $\gamma_{des}(t)$ is the probability that each of the n molecules is desorbed and it is a function of time, as we will see below.

The other addendum $(n_{max}-n(t))\gamma_{abs}(t)$ represents the rate of absorption, that is, in the same fashion, given by the product of a probability and a number of particles. We define n_{max} as the number of particles that realize a complete coverage on the surface, thus $(n_{max} - n(t))$ represents how much space is available on the surface for absorption, measured in particle units. The probability to have a random gas particle landing on the surface is proportional to this space.

As mentioned above, these probabilities γ_{des} and γ_{abs} may not be constant, but depend on, for example, time variable gas pressure, accordingly to a linear relation:

$$\begin{aligned} \gamma_{abs} &= \alpha_{abs}(g_{mx}^{abs} - g_{mn})P + g_{mx} \\ \gamma_{des} &= \alpha_{des}(g_{mn}^{des} - g_{mn})P + g_{mx} \end{aligned} \tag{3}$$

where g_{mx} and g_{mn} are two offsets that represent the range of pressure and α is the coefficient that fit the experimental data. In the differential equation (2), the first term on the right is clearly an exponential decay, whereas the second is a $(1 - e^{-x})$ type growth, so the three equations (1), (2) and (3) altogether result in a growth or an exponential decay behavior depending on the pressure parameter.

If we integrate numerically the differential equation (2) and run a simulation with the experimental variable pressure data inserted in equation (3) we obtain the result in figure 7 that is strikingly similar to the behavior found in the experiments suggesting that is a dynamically changing coverage of spurious gas molecules absorbed on the surface that causes the photoluminescence variations observed experimentally.

This study wants to show and describe systematically for the first time the influence of Gas pressure on the luminosity of InGaN devices. The phenomena is also successfully modeled and possible mechanisms are briefly described.

4. Conclusions

We describe systematically for the first time the influence of Gas pressure on the luminosity of InGaN devices. The phenomena is also successfully modeled and possible mechanisms are briefly described. We found that photoluminescence has lower intensity and shows unevenly distributed intense luminous centers{5} (bright spots) and blinking points when the level of absorption coverage is high on the sample surface. In contrast, when vacuum is drawn and spurious gas particles are desorbed, sample surface emission has higher intensity and it is homogeneous, with almost no bright spots or blinking points. By what mechanism the light emission is reduced is not clear, oxygen influence may reach the barrier through dislocations and trap carriers to passivate those centers responsible for the luminescence at the interface. However, what is exactly happening on the surface is at this stage still speculative. We cannot go beyond that without further throughout experiments and tests that will involve another complete research paper that we are preparing. We speculate that unstable blinking and the so called optical memory effect are caused by absorbed material on the surface of the sample. In particular, the presence of O_2 in the proximity of the surface, induce adsorption that influence the excitation of GaN layers, not not only the InGaN layer. Since this decreased luminosity effect with pressure happens only at 365nm and not 405nm, the phenomenon is taking places by carriers that are are excited deep in the barrier. In our sample the capping layer is extremely thin (3-5 nm), oxygen influence may reach the barrier through dislocations and trap carriers to passivate those centers responsible for the luminescence at the interface. Our molecular coverage model fits the experimental curves that relate the ambient pressure and the sample photo-luminescence, suggesting that coverage dynamic is the main driving force of the phenomenon.

This study wants to contribute to the understanding of fundamental processes involved in the emission phenomena of InGaN materials and to help to break ground to improve the efficiency and reliability of next generation nitride semiconductor devices.

This study was partially supported by the Japanese grant KAKEN (project number 24560014) and by the Yokohama City University Sabbatical fund 2015-2016.

References:

[1] S. Strite, H. Morkoç, Gallium nitride, aluminum nitride and indium nitride: A review, Journal of Vacuum Science and Technology, B 10 (1992) 1237–1266.

[2] A. Shikanai, T. Azuhata, T. Sota, S. Chichibu, A. Kuramata, K. Horino, S. Nakamura, Biaxial strain dependence of exciton resonance energies in wurtzite GaN., Journal of Applied Physics 81 (1997) 417 – 424.

[3] A. Kaneta, M. Funato, Y. Narukawa, T. Mukai, Y. Kawakami, Direct correlation between nonradiative recombination centers and threading dislocations in InGaN quantum wells by near-field photoluminescence spectroscopy, physica status solidi (c) 3 (2006) 1897–1901. 74.

[4] T. S. Zheleva, O. H. Nam, M. D. Bremser, R. F. Davis, Dislocation density reduction via lateral epitaxy in selectively grown GaN structures, Applied Physics Letters 71 (1997) 2472–2474.

[5] R. Micheletto, N. Yoshimatsu, A. Kaneta, Y. Kawakami, S. Fujita, Indium Concentration on PL Spatial inhomogeneity in InGaN Single Quantum Well Structures detected by an original low cost near-field probe, Applied Surface Science 229 (2004) 338–345.

[6] Y. Narukawa, Y. Kawakami, Role of self-formed InGaN quantum dots for exciton localization in the purple laser diode emitting at 420 nm, Applied Physics Letters 70 (1997) 981.

[7] K. Oikawa, C. Feldmeier, U. T. Schwarz, Y. Kawakami, R. Micheletto, Real-time near-field evidence of optical blinking in the photoluminescence of InGaN by scanning near-field optical microscope, Optical Material Express 1 (2011) 158–163.

[8] R. Micheletto, M. Abiko, A. Kaneta, Y. Kawakami, Y. Narukawa, T. Mukai, Observation of optical instabilities in the photoluminescence of ingan single quantum well., Applied Physics Letters 88 (2006) 061118.

[9] C. Feldmeier, M. Abiko, U. T. Schwarz, Y. Kawakami, R. Micheletto, Transient memory effect in the photoluminescence of InGaN single quantum wells, Optics Express 17 (2009) 22855–22860.

[10] S. Chichibu, T. Azuhata, T. Sota, S. Nakamura, Spontaneous emission of localized excitons in InGaN single and multiquantum well structures., Applied Physics Letters 69 (1996) 4188 – 4190.

[11] M. Nirmal, B. Dabbousi, M. Bawendi, J. Macklin, J. Trautman, T. Harris, L. Brus, Fluorescence intermittency in single cadmium selenide nanocrystals, Nature 383 (1996) 802–804.

[12] A. Yoshikawa, S. B. Che, W. Yamaguchi, H. Saito, X. Q. Wang, Y. Ishitani, E. S. Hwang, Proposal and achievement of novel structure InN/GaN multiple quantum wells consisting of 1 ML and fractional monolayer InN wells inserted in GaN matrix, Applied Physics Letters 90 (2007) 073101.

[13] J. Seufert, M. Obert, R. Weigand, T. Kuemmell, G. Bacher, A. Forchel, K. Leonardi, D. Hommel, Correlated temporal fluctuations and random intermittency of optical transitions in a single quantum dot., Phys. Status Solidi B 224 (2001) 201205.

[14] N. Kaufmann, Ph.D. thesis, Ecole Polytechnique de Losanne, 2013.

[15] B. Zhang, Y. Li, T. Yasuda, W. Wang, Y. Segawa, K. Edamatsu, T. Itoh, Intermittent photoluminescence and thermal ionization of ZnCdSe/ZnSe quantum dots grown by molecular beam epitaxy, Applied Physics Letters 73 (1998) 1266–1268.

[16] P. E. D. Soto Rodriguez, V. J. Gomez, P. Kumar, E. Calleja, R. Noetzel, Near-infrared InN quantum dots on high-In composition InGaN, Applied Physics Letters 102 (2013).

[17] D. Bertram, M. Hanna, A. Nozik, Two color blinking of single strain-induced GaAs quantum dots, Applied Physics Letters 74 (1999) 2666–2668.

[18] J. L. Lyons, A. Janotti, C. G. Van de Walle, Carbon impurities and the yellow luminescence in GaN, Applied Physics Letters 97 (2010) 152108.

[19] M. Kuno, D. Fromm, A. Gallagher, D. Nesbitt, O. Micic, A. Nozik, Fluorescence intermittency in single InP quantum dots, Nano Letters 1 (2001) 557–564.

[20] M. Sugisaki, H. Ren, K. Nishi, Y. Masumoto, Optical properties of InP self-assembled quantum dots studied by imaging and single dot spectroscopy, Japanese Journal of Applied Physics 41 (2002) 958–966. 13th International Conference on Indium Phosphide and Related Materials (IPRM), Nara, Japan, May 14-18, 2001.

[21] X. M. Duan, C. Stampfl, Defect complexes and cluster doping of InN: First-principles investigations, Physical Review B 79 (2009).

[22] A. Janotti, C. G. Van de Walle, Sources of unintentional conductivity in InN, Applied Physics Letters 92 (2008) 032104.

[23] R. Micheletto, K. Oikawa, C. Feldmeier, Observation of lattice thermal waves interference by photoluminescence blinking of InGaN quantum well devices, Applied Physics Letters 103 (2013) 17109.

[24] C. Van de Walle, J. Neugebauer, First-principles calculations for defects and impurities: Applications to III-nitrides, Journal of Applied Physics 95 (2004) 3851–3879.

[25] G. Staszszak, I. Gorczyca, T. Suski, X. Wang, N. Christensen, A. Svane, E. Dimakis, T. Moustakas, Journal of Applied Physics 113 (2013) 123101.

[26] S. Pearton, H. Cho, J. LaRoche, F. Ren, R. Wilson, J. Lee, Applied Physics Letters 75 (1999) 2939.

[27] G. Alfieri, T. Tsutsumi, R. Micheletto, Electronic properties of substitutional impurities in ingan monolayer quantum wells, Applied Physics Letters 106 (2015) 192102.

[28] M. J. Kappers, T. Zhu, S.-L. Sahonta, C. J. Humphreys, R. A. Oliver, SCM and SIMS investigations of unintentional doping in III-nitrides, physica status solidi (c) 12 (2015) 403–407.

[29] M. S. Miao, Q. M. Yan, C. G. Van de Walle, Electronic structure of a single-layer InN quantum well in a GaN matrix, Applied Physics Letters 102 (2013) 102103.

[30] P. G. Moses, M. Miao, Q. Yan, C. G. Van de Walle, Hybrid functional investigations of band gaps and band alignments for AlN, GaN, InN, and InGaN, Journal of Chemical Physics 134 (2011) 084703.

[31] C. C. Yang, J. K. Sheu, C. H. Kuo, M. S. Huang, S. J. Tu, F. W. Huang, M. L. Lee, Y.-H. Yeh, X. W. Liang, W. C. Lai, Improved Power Conversion Efficiency of InGaN Photovoltaic Devices Grown on Patterned Sapphire Substrates, IEEE Electron Device Letters 32 (2011) 536–538.

[32] N. Okada, K. Tadatomo, K. Yamane, H. Mangyo, Y. Kobayashi, H. Ono, K. Ikenaga, Y. Yano, K. Matsumoto, Performance of InGaN/GaN light-emitting diodes grown using NH 3 with oxygen-containing impurities, Japanese Journal of Applied Physics 53 (2014) 081001.

Figure Captions:

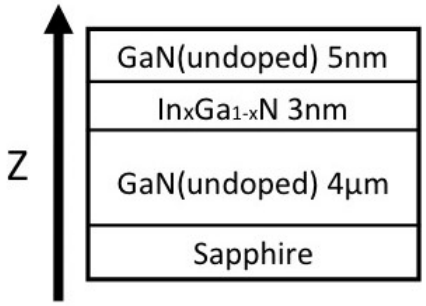

Figure 1: The structure of our sample. A 4 mm sapphire substrate is at the base of a layer of undoped GaN (4 μ m), an active layer of InGaN 3 nm thick and a final 5 nm capping layer of undoped GaN.

280

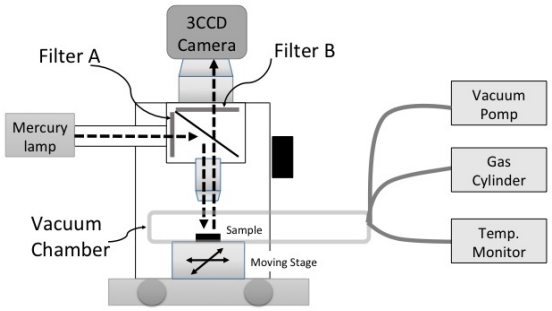

Figure 2: The scheme of our microscope. A mercury lamp is filtered by the filter A to select the excitation wavelength (λ=405 nm or λ=365 nm). A second colored filter in B is used to cut away the excitation signal and collect only the photoluminescence (the filter is centered about λ=500nm). Sample is held in a thermally controlled holder enclosed in a vacuum chamber connected to various gas cylinders.

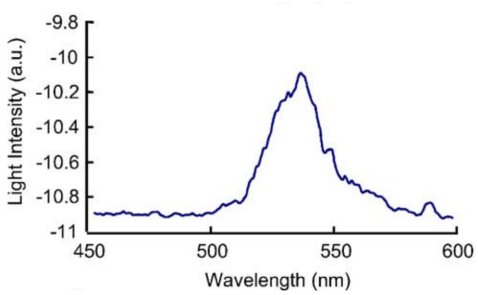

Figure 3: The bulk emission of the sample, taken in near-field optics conditions (from Micheletto et al. {5})

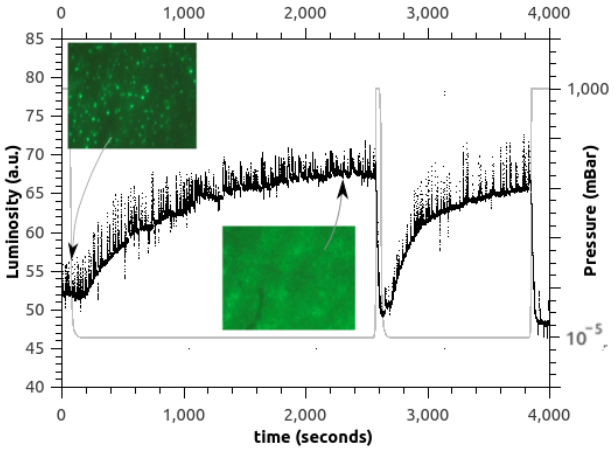

Figure 4: The luminosity time dependence when sample is subject to pressure changes. The gray line represent air pressure, that initially is kept at 1000 mBar and then drawn to 10^{-5}mBar by a vacuum pump. As soon as the pressure drops, photoluminescence slowly grows up to 150% the initial value. In the insets are images of the sample's surface. They are taken on the same spot but in different pressure conditions (as indicated by the arrows, at the beginning $t = 0$ and at about $t = 2200$ secs). The difference in emission pattern is impressive, not only the overall luminosity is increased, but intense luminous centers and blinking points are much less prominent or disappeared completely. Excitation wavelength is 365 nm, photoluminescence is filtered by a 500nm color filter and it is centered around 540nm. The same test is repeated twice in this recording to show reproducible behavior.

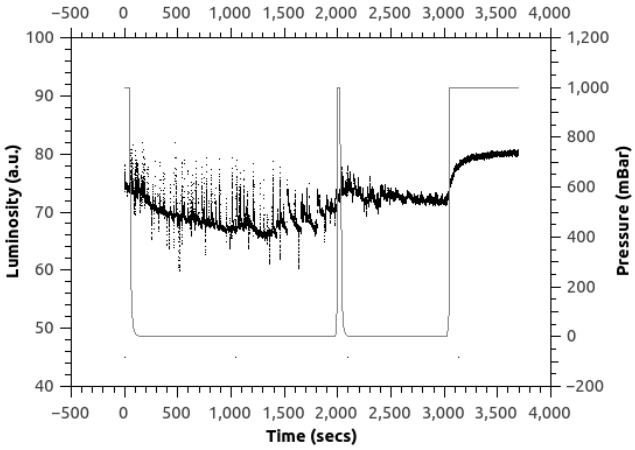

Figure 5: The profile of luminosity of a sample excited with 405nm and exposed to variation of pressure in air. The experiment is performed in the same conditions as in figure 4.

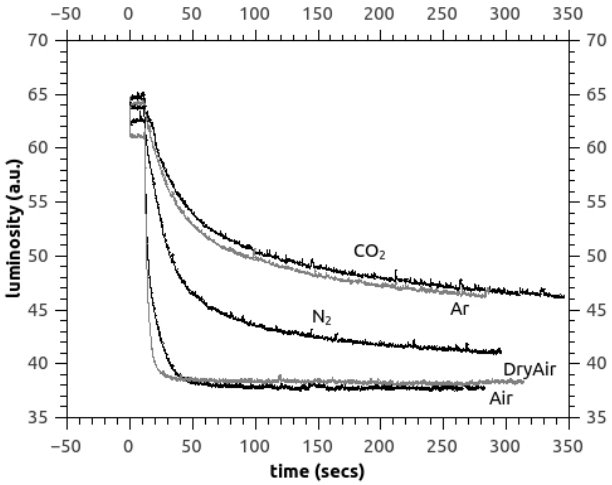

Figure 6: The decay of luminosity when a InGaN sample is brought from high vacuum to atmospheric pressure with different gases. The gases containing Oxygen show the most prominent influence.

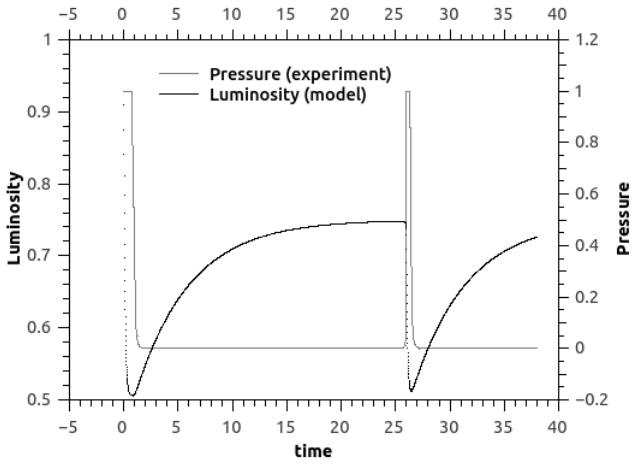

Figure 7: A simulation of $n_{max} = 1000$ molecules for the model described in equation (2) and equation (3). The continue curve represent the pressure obtained from experimental data, and the dotted profile is the simulation of the luminosity. We integrated using an Eulero method with time step $dt = 0.01$ seconds, γ_{abs} and γ_{des} were set to 3 and 0.1 respectively. Other parameters in equations (1), (2) and (3) were $I_{max} = 1$, $\beta = 5 * 10^{-4}$, $g_{mx}^{abs} = 3$, $g_{mx}^{des} = 0.1$ and $g_{mn} = 0.1$. Vertical axis for luminosity is in arbitrary units, for pressure is Atmosphere. Horizontal axis is time in seconds. The pressure values are real data taken from the experiment.