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GaN surface as the source of non-radiative defects in InGaN/GaN quantum wells

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Blue light-emitting diodes based on III-nitride semiconductors are nowadays widely used for solid-state lighting. They exhibit impressive figures of merit like an internal quantum efficiency close to 100%. This value is intriguing when considering the high dislocation density running throughout the InGaN/GaN quantum well (QW) active region. This striking feature is currently ascribed to carrier localization occurring in the InGaN alloy, which hinders their diffusion toward non-radiative recombination centers. However, it was recently reported that another source of defects, disconnected from dislocations, dramatically decreases the radiative efficiency of InGaN/GaN QWs. Those defects, present at the surface, are usually trapped in an InGaN underlayer (UL), which is grown before the QW active region. To get insight into the trapping mechanism we varied the UL thickness, In content, and materials system (InGaN or InAlN) and studied the photoluminescence decay time at 300 K of a single InGaN/GaN QW. Our data demonstrate that nearly two defects are incorporated for three indium atoms whatever the UL materials. In addition, we show that those defects are created during the high-temperature growth of GaN and that they segregate at the surface even at low-temperature. Eventually, we propose an intrinsic origin for these surface defects.

III-nitride white light-emitting devices (LEDs), which consist of a blue LED covered by a yellow phosphor recently achieved a record luminous efficacy of 300 lm/W.[1] This spectacular performance must be credited to InGaN/GaN quantum wells (QWs), which form the active region of blue LEDs. When S. Nakamura reported the first high-brightness InGaN based LED,[2] the scientific community was astonished since the device grown on sapphire was full of dislocations (density $> 10^9 cm^{-2}$), which act as non-radiative recombination centers (NRCs).[3] The defect-insensitivity of InGaN/GaN QWs was then ascribed to the intrinsic properties of InGaN alloy: carrier are strongly localized due to large potential fluctuations induced by random alloy disorder[4] hindering their diffusion towards NRCs.[5] Besides dislocations, point defects such as impurities or vacancies are another common source of NRCs in semiconductor optoelectronic devices. In this vein, Armstrong *et al.* pointed out the detrimental impact of deep level defects on the efficiency of blue LEDs.[6] In particular, they showed that the density of NRCs in InGaN/GaN QWs decreases if an InGaN thick layer is deposited before the growth of the active region. In fact such an InGaN underlayer (UL), or InGaN/GaN superlattice, is commonly used in high efficiency commercial blue LEDs grown by metal-organic chemical vapor deposition (MOCVD). Its role is to trap surface defects (SDs) and avoid their further incorporation into the InGaN/GaN active region.[6–8] It was also noticed that this effect holds when InGaN QWs are grown on free-standing GaN substrates, which indicates that dislocations are not at play.[7]

In this study, we show that the defects burried in the InGaN UL are intrinsic to the GaN surface. They form at high temperature ($> 900°$C) and segregate at the surface even for low growth temperatures ($< 800°$C). In turn, they are incorporated in indium containing layers (InGaN or InAlN) where they create NRCs.

Samples were grown by MOCVD either in a vertical Aixtron 3x2" CCS system (reactor 1) or a horizontal Aixtron 200/4 RF-S system (reactor 2). Substrates are *c*-plane sapphire (dislocation density of about $10^9 cm^{-2}$) or c-plane freestanding (FS) GaN (dislocation density $\sim 10^6 cm^{-2}$). The common structure for all the samples is a GaN buffer, an InGaN (InAlN) UL, a GaN spacer, an InGaN single (S)QW and a GaN cap of 50 nm. The buffer is grown using trimethylgallium (TMGa) and H_2 as carrier gas at a temperature of 1000°C. For the growth of the InGaN (InAlN) alloy, the GaN spacer and the GaN cap, the carrier gas is switched to N_2. The InGaN UL is grown using trimethylindium (TMIn) and triethylgallium (TEGa) at a temperature of 770°C. The InAlN UL is grown using TMIn and trimethylaluminum (TMAl) at a temperature of 750°C. The SQW growth temperature is $750 - 755°$C, the indium composition 12% and the thickness 2.7 nm. Time-resolved photoluminescence (TRPL) was performed using a streak camera operating in synchroscan mode. We used the third harmonic of a mode-locked Ti:sapphire laser emitting at 280 nm as excitation source. The pulse width is 2 ps and the repetition rate is 80.5 MHz. To extend the time window for long PL decay times, we used a pulse picker. For the InGaN QWs, the spectral window corresponds to the QW emission. Time-integrated PL (TIPL) was performed with the same excitation source as TRPL but the signal was integrated over several pulses (with an excitation power density of 0.26 W/cm^2).

As shown in previous reports,[6–8] the role of InGaN UL in an LED structure is to burry SDs and ensure high efficiency InGaN/GaN active region. We first study

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the capture mechanism of these SDs by the InGaN UL. For that purpose, we grew a series of identical 2.7 nm $In_{0.12}Ga_{0.88}N$/GaN single SQWs (Series A) except for the thickness (d) of the $In_{0.03}Ga_{0.97}N$ UL, which was varied from 0 to 214 nm. PL measurements were performed at room temperature with a low exciation power density (0.26 W/cm^2). The PL intensity increases by more than two orders of magnitude between a bare SQW sample (without UL) and the SQW with an UL of 214 nm (Fig. 1(a)). The intensity first increases with the thickness and then saturates. One can also notice a slight red-shift of both the SQW and the UL emission energy for thick ULs, which might be ascribed to strain-dependent In incorporation.[9] Interestingly, the PL intensity of the InGaN UL also gets higher (see SM).

Additionally, we carried out TRPL experiments at 300 K to measure the QW effective lifetime and get insight into non-radiative (NR) processes. In agreement with the PL intensity behavior, the effective lifetime exhibits a huge improvement when the UL thickness increases (Fig. 1(b)). From 170 ps when no UL is inserted, it goes up to 20 ns for the thickest one. Notice that the nonexponential behavior at long delays has already been observed in InGaN/GaN QWs grown on bulk GaN substrates and ascribed to the saturation of slow dynamics NRCs.[10]

The dependence of the InGaN/GaN SQW optical properties with the thickness of the InGaN UL suggests the following mechanism: SDs are incorporated if In atoms are present at the surface and, once buried in InGaN layers, they create NRCs. This accounts well with former results, which showed, for instance, a strong improvement of the optical properties of multiple (M) QW structures compared to SQW.[11–13] Indeed, in this case, the first QWs in the MQW structure play the role of the InGaN UL by trapping SDs.

To account for the evolution of the QW decay time as a function of the InGaN UL thickness, we developed a model where the NR lifetime is a function of the SD concentration in the InGaN/GaN QWs.[14] First, we suppose that SDs segregate at the surface, with a surface concentration given by $[SD] = \theta_0 R^N$, where θ_0 is the initial surface density after the GaN growth at high temperature, N is the number of monolayers (ML) deposited ($N = d/e_{\mathrm{ML}}$ with e_{ML} the InGaN ML thickness), and R the segregation coefficient.[15] Previous observations by Akasaka *et al.*[8] indicate that incorporation of SDs in GaN is negligible, i.e R is close to 1. In contrast, SDs are incorporated in InGaN layers, i.e. R decreases. Assuming that SDs are buried upon interaction with In atoms, we can write $R = R_{\mathrm{GaN}} - xp$ with R_{GaN} the segregation of SDs in GaN, x the In composition of the InGaN layer, and p the interaction efficiency between In atoms and SDs. Then we express the effective lifetime of the QW as: $1/\tau_{\mathrm{eff}} = 1/\tau_0 + 1/\tau_{\mathrm{NR,SD}}$, with τ_0 the QW lifetime when SDs are all trapped into the InGaN UL, and $\tau_{\mathrm{NR,SD}}$ the NR lifetime induced by the incorporation of SDs. The latter is given by: $1/\tau_{\mathrm{NR,SD}} \propto [SD]_{\mathrm{QW}}$, with $[SD]_{\mathrm{QW}}$ the concentration of SDs in the QW. Finally, the QW

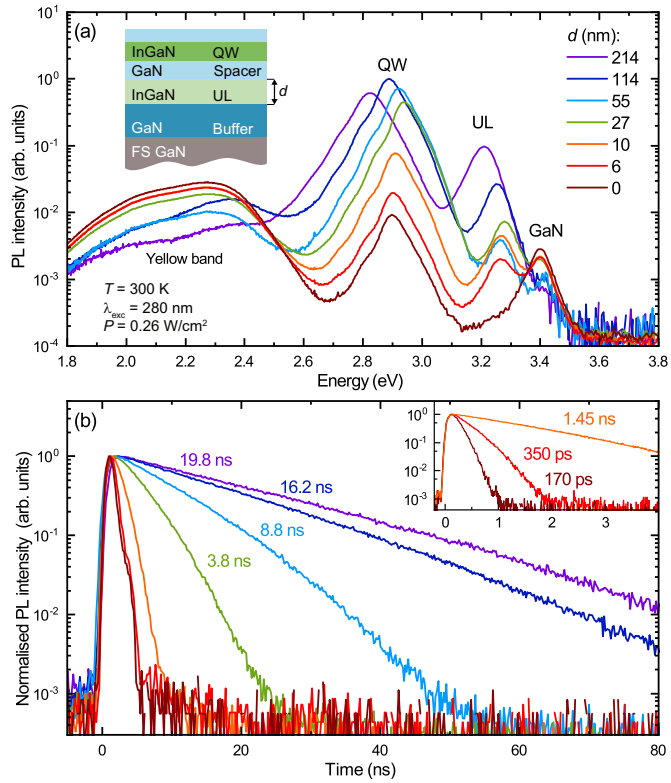

FIG. 1. (a) PL spectra recorded at 300 K for different InGaN UL thicknesses. (b) Corresponding normalized PL decay traces for a 80 ns time window and, Inset, for a time window of 4 ns.

effective lifetime can be expressed as:

$$\tau_{\mathrm{eff}} = \tau_0 \frac{1}{1 + \tau_0 \alpha (R_{\mathrm{GaN}} - xp)^N} \quad (1)$$

with α, a constant, which depends on θ_0 and the electron-hole capture coefficient of the NR defect (see SM). The experimental effective lifetime as a function of the InGaN UL thickness are fitted using Eq. 1 (Fig. 2(a), green line). The value for τ_0 is 18 ns, which is measured for a 214 nm thick InGaN UL. The composition and the thickness are measured by high resolution x-ray diffraction (HR-XRD) analysis. The best fit is obtained with an interaction efficiency of 0.7 ($R = 0.9782$), which confirms the strong interaction of SDs with indium.

Next, a set of InGaN/GaN SQW samples (Series B) was prepared keeping constant the InGaN UL thickness (55 nm) but varying the In content (up to 16% to ensure pseudomorphic layer). It is worth noticing that we used another reactor (horizontal reactor) and the substrate was sapphire. The InGaN UL was deposited under slightly different growth conditions ($T_g = 750°$C with H_2 and N_2 used as carrier gases). The QW effective lifetimes for this sample series are displayed in Fig. 2(b). Eq. (1) still with $p = 0.7$ reproduces well the QW effective lifetime. Note that τ_0 is 3.3 ns, which is smaller than the value measured on FS GaN substrate, which might be

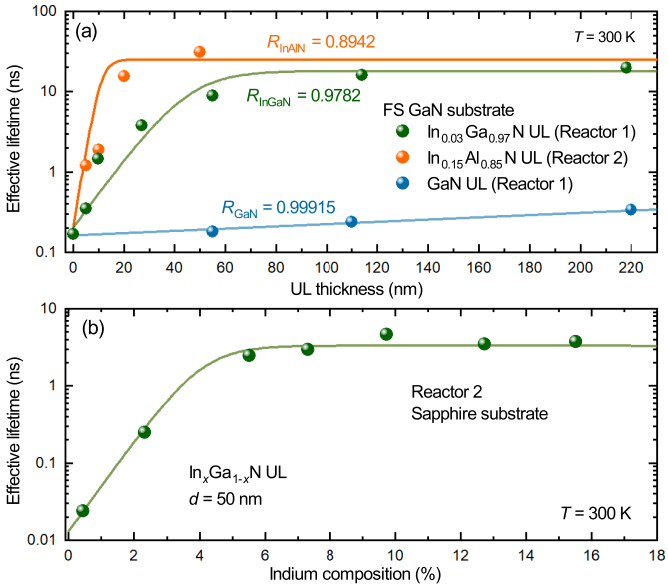

FIG. 2. (a) Effective lifetime as a function of UL thickness for three different materials: InGaN UL in green (Series A), GaN UL in blue (Series D) and InAlN UL in orange (Series C). (b) Effective lifetime as a function of InGaN UL composition (Series B). The dots are experimental data and the lines are fits based on Eq. (1) using an interaction efficiency $p = 0.7$.

due to a higher dislocation density. A piece of information is that SDs are present whatever the reactor type: vertical design with stainless steel showerhead for reactor 1 or horizontal design with quartz liner (no stainless steel) for reactor 2.

We then checked whether SD trapping is specific to InGaN layers. To this end, we prepared a series of InGaN/GaN SQWs grown on FS-GaN substrate with $In_{0.15}Al_{0.85}N$ UL (series C). Notice that the $In_{0.15}Al_{0.85}N$ alloy is under slight tensile strain for this composition.[16] The PL decay time of the InGaN/GaN SQWs dramatically increases with the InAlN UL thickness (Fig 2(a)). Due to the high indium content in the InAlN layer, the thickness needed to reach the saturation of the effective lifetime is only 20 nm. The data in Fig. 2(a) were fitted with Eq. (1) with $p = 0.7$ ($R = 0.8942$), as for InGaN UL. To further emphasize the critical role of indium, we grew an additional series of InGaN/GaN SQW samples where the UL was replaced by a pure GaN layer grown at 770°C (series D). The PL decay time exhibits a slight increase with GaN thickness (Fig. 2(a)). Fitting the data with Eq. (1) (with $x = 0$) leads to $R_{GaN} = 0.99915$. This high R value confirms the strong surface segregation of SDs in GaN even at a growth temperature as low as 770°C. Consequently, 2 μm of GaN grown at 770°C would be required to trap all SDs. This highlights the need of indium in the UL, as already pointed out by Akasaka *et al.*[8]

Although the phenomenological model we propose accounts well for the dependence of the QW effective lifetime on the InGaN (InAlN) UL thickness or composition, it does not provide any insights into the nature of those SDs. In the literature, capture coefficients for impurities and complexes range between 10^{-6} and 10^{-8} $cm^3 s^{-1}$,[17–20] corresponding to impurity densities comprised between 10^{15} and $10^{17} cm^{-3}$.

We carried out secondary ion mass spectrometry (SIMS) and searched for Fe, Ca, O, C, Mg, which are supposed to be detrimental to the radiative efficiency of InGaN QWs.[17,21–25] SIMS measurements did not allow us establishing any straightforward relationship between those impurities and the QW effective lifetime. However, one could argue that the SIMS detection limit was too high (around 10^{16} cm^{-3}) or that we missed the relevant impurity.

Based on previous results, SDs should have the following properties: (i) once incorporated into InGaN layers they create efficient NRCs, (ii) they strongly interact with indium atoms, and (iii) their concentration should range between 10^{15} and 10^{17} cm^{-3}. Another intriguing observation is that SDs are present whatever the MOCVD growth reactor type. It is also a common feature that InGaN/GaN SQWs grown without InGaN UL exhibit a poor radiative efficiency.[11–13] We therefore postulate that SDs could not be impurities but rather intrinsic point defects, which form during the growth of GaN at high temperature.

To investigate the dependence of the density of SDs on growth temperature, we prepared a new series (Series E) of InGaN/GaN SQW samples with InGaN UL, but with a GaN spacer deposited at various temperatures T_{GaN} (Fig. 3). Increasing the growth temperature T_{GaN} from 770°C to 1020°C leads to a rapid collapse of the QW PL intensity (Fig. 3). The effective lifetimes measured at 300 K are displayed in log scale as a function of $1000/T_{GaN}$ (Inset, Fig. 3). Using the previous model and assuming that the SD density θ_0 scales as $\exp\left(-\frac{E_a}{k_B T_{GaN}}\right)$, we extracted an activation energy of 3.6 eV. Interestingly, this value is close to the activation energy reported in the literature for the decomposition of GaN.[26,27]

The dependence of the SD density on growth temperature suggests intrinsic point defects whose creation rate might be enhanced at the GaN near surface region. Indeed, the defect formation energy may be significantly different from the bulk formation energy.[28] In addition, vacancies tend to diffuse towards the surface, as observed in other materials.[29]

We could thus infer that the GaN surface and near surface region provide a reservoir of point defects, which segregate at the surface until they react with indium atoms. Once buried, due to the interaction with indium, they form NRCs.

Let us consider the most likely points defects, which are gallium and nitrogen vacancies. Gallium vacancies (V_{Ga}) in GaN epilayers grown by MOCVD have been discussed back to 1996 and proposed to be responsible for the yellow-band luminescence.[30] In GaN homoepitaxial layers, two energy levels associated to V_{Ga} com-

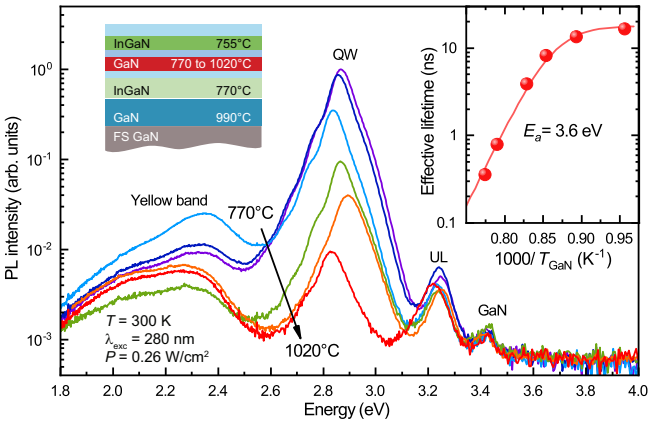

FIG. 3. PL spectra recorded at 300 K for a sample with a spacer grown at different temperatures (T_{GaN}). Inset: InGaN SQW effective lifetime (red points) as a function of $1000/T_{\mathrm{GaN}}$. The red line corresponds to the calculated effective lifetimes assuming thermally activated SDs ($E_a = 3.6$ eV).

plexes have been determined by deep level spectroscopy: $E_c - 0.56$ eV and $E_c - 0.23$ eV.[31] These values are far from the energy level $E_c - 1.62$ eV that was identified to be related to the creation of NRCs by SDs in InGaN/GaN QWs.[6] Recently, theoretical calculations have pointed out that V_{Ga} are unlikely in bulk GaN, but instead complexes with oxygen and hydrogen are.[20,32] This would mean that oxygen and hydrogen could be detected by SIMS if their density were high enough, which is not the case in our samples (see SM). In addition, Dreyer *et al.* computed the impact of these V_{Ga} complexes on NR recombinations in InGaN layer and found that they play a marginal role below 15% In content.[20] Thus V_{Ga} and related complexes are not expected to dramatically impact the efficiency of the present InGaN/GaN QWs, which have an indium content of 12%.

It is commonly admitted that the concentration of nitrogen vacancies (V_N) in bulk GaN is very low due to their large formation energy.[28] However, the formation energy of vacancies at semiconductor surface may be significantly smaller.[33] It was also proposed that during the decomposition of GaN, nitrogen atoms dissociate from the surface and form N_2 molecules, leading to a nitrogen-poor growth front, which could be a source of V_N.[27,34,35] Therefore, if $[V_N]$ is low in bulk GaN, this might be no longer the case at the GaN surface. Notice that the predominance of anion vacancies near the surface was already pointed out in common III-V semiconductors.[33]

The present study points out the strong affinity of SDs with indium atoms. A theoretical study predicts that the formation energy of V_N in the presence of indium is decreased.[36,37] Therefore, the scenario could be the following: V_N are created near the surface during high temperature growth of GaN. Once formed, they segregate at the surface even for LT growth GaN due to their high formation energy in bulk GaN.[38] In the presence of indium atoms, the segregation process is quenched: V_N are incorporated in the bulk due to a decrease of their formation energy in InGaN. This is consistent with the formation of stable V_N and In complexes as theoretically predicted.[39,40]

In conclusion, we studied the origin of surface defects in GaN, which dramatically reduce the efficiency of InGaN/GaN QWs. We proposed that the rather low stability of GaN at high temperature induces nitrogen vacancies at the surface. Those V_N strongly segregate, even during low-temperature growth of GaN. In contrast, V_N are incorporated in indium containing layers (InGaN or InAlN), where they create NRCs. We thus propose that the role of the InGaN UL is to capture preexisting V_N at the GaN surface. Hence, our results shed new light on the physics and fabrication of high performance III-nitride based optoelectronic devices.

SUPPLEMENTARY MATERIAL

See supplementary material for complementary information.

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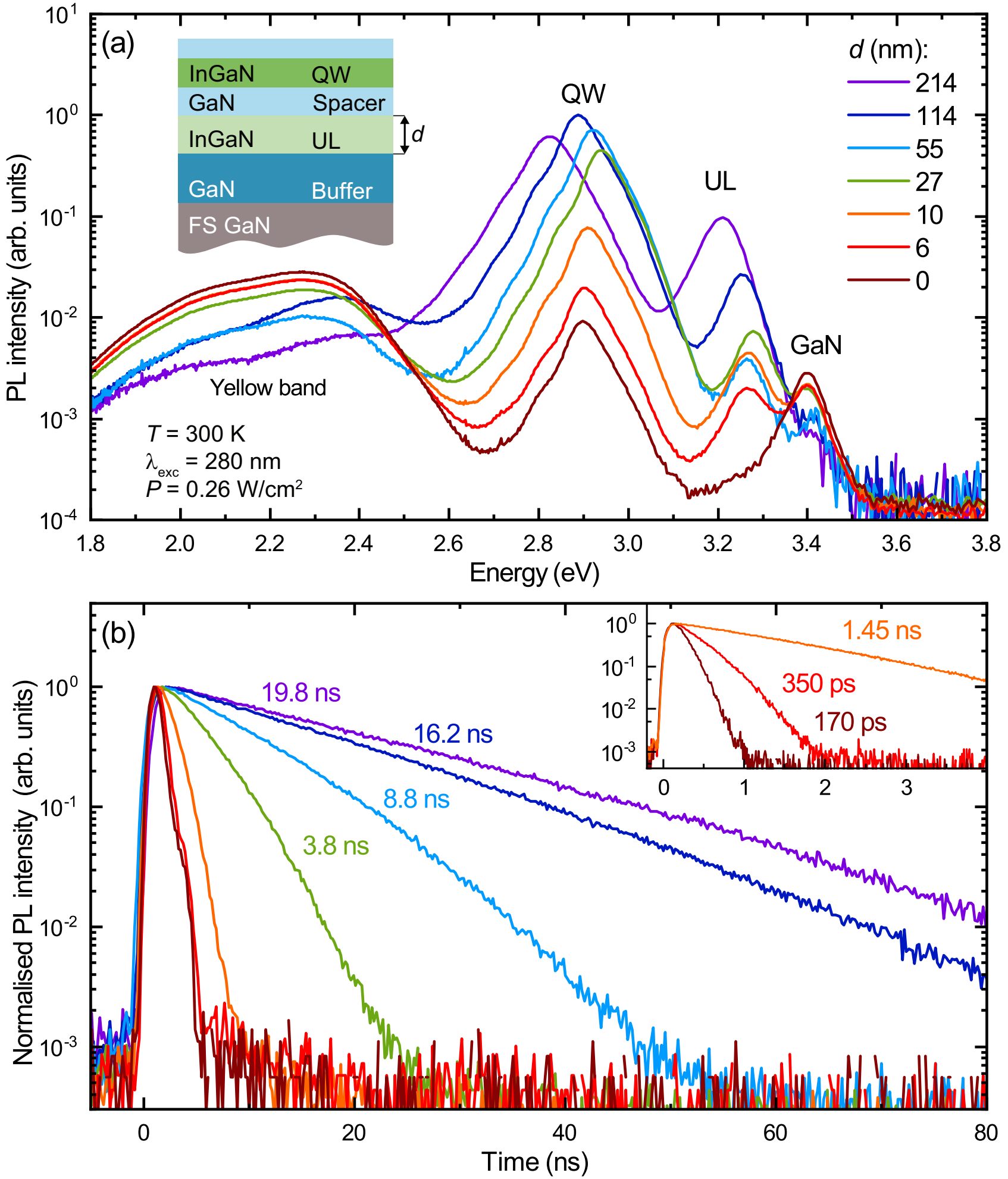
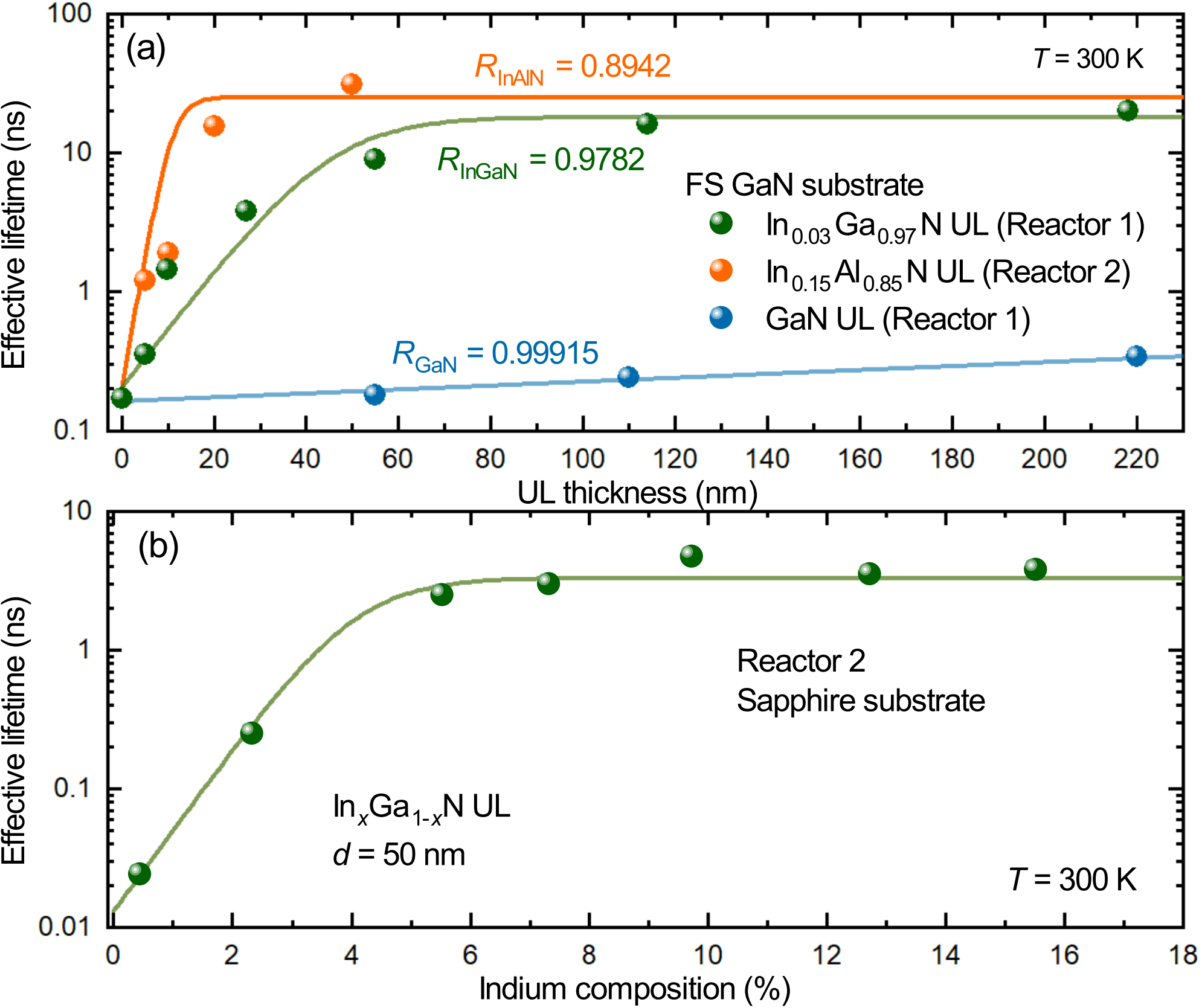
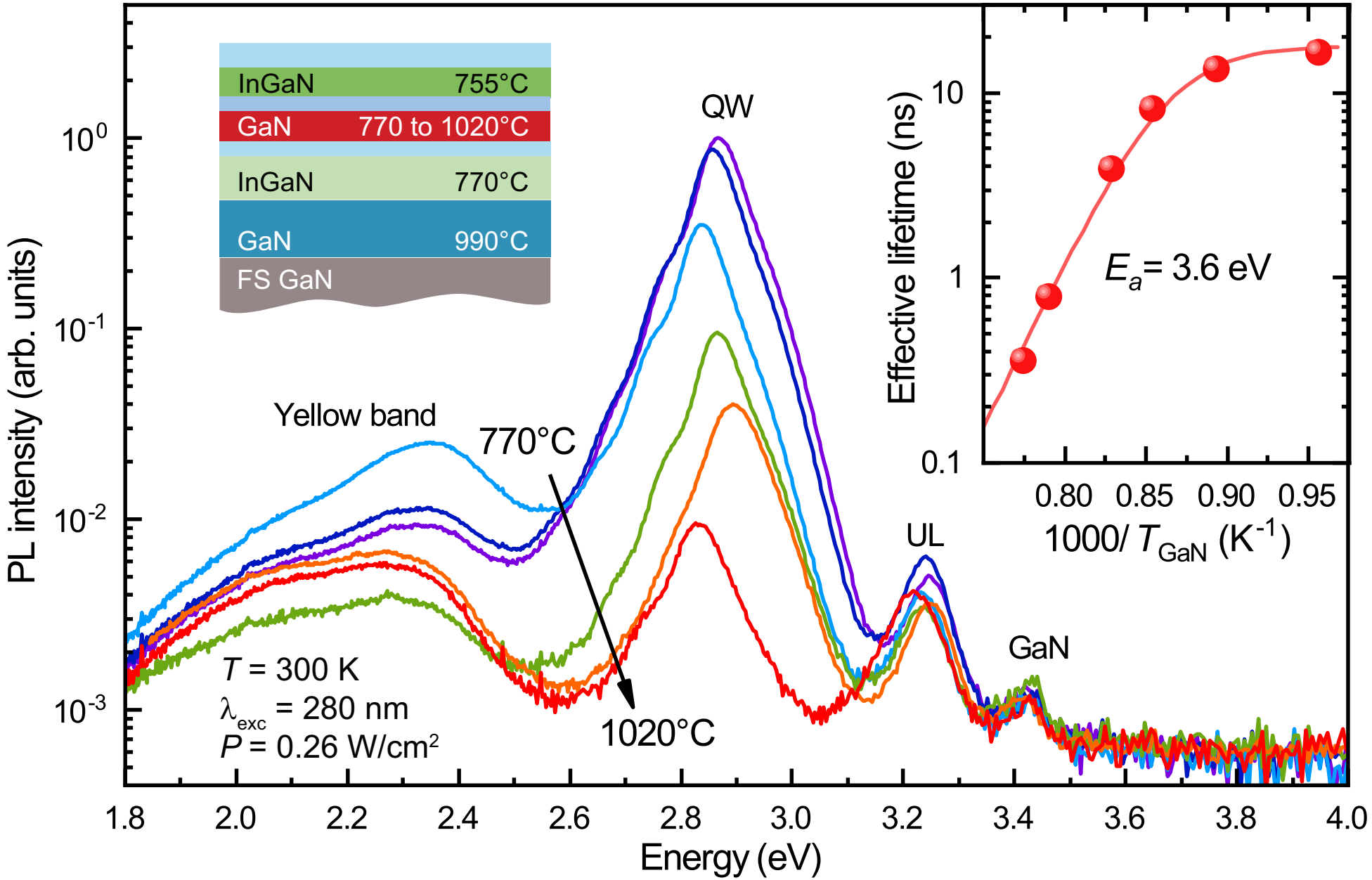

(a)
InGaN QW
GaN Spacer
InGaN UL
GaN Buffer
FS GaN
d
d (nm):
214
114
55
27
10
6
0
QW
UL
GaN
Yellow band
T = 300 K
λexc = 280 nm
P = 0.26 W/cm²
PL intensity (arb. units)
Energy (eV)
(b)
19.8 ns
16.2 ns
8.8 ns
3.8 ns
1.45 ns
350 ps
170 ps
Normalised PL intensity (arb. units)
Time (ns)


(a)
T = 300 K
R_InAlN = 0.8942
R_InGaN = 0.9782
R_GaN = 0.99915
FS GaN substrate
In0.03Ga0.97N UL (Reactor 1)
In0.15Al0.85N UL (Reactor 2)
GaN UL (Reactor 1)
Effective lifetime (ns)
UL thickness (nm)
(b)
Reactor 2
Sapphire substrate
InxGa1-xN UL
d = 50 nm
T = 300 K
Effective lifetime (ns)
Indium composition (%)


InGaN 755°C
GaN 770 to 1020°C
InGaN 770°C
GaN 990°C
FS GaN
QW
Yellow band
770°C
1020°C
UL
GaN
T = 300 K
λexc = 280 nm
P = 0.26 W/cm2
PL intensity (arb. units)
Energy (eV)
Effective lifetime (ns)
Ea= 3.6 eV
1000/ TGaN (K-1)