

# Supporting Information

## Carrier Recombination Processes in GaAs Wafers Passivated by Wet Nitridation

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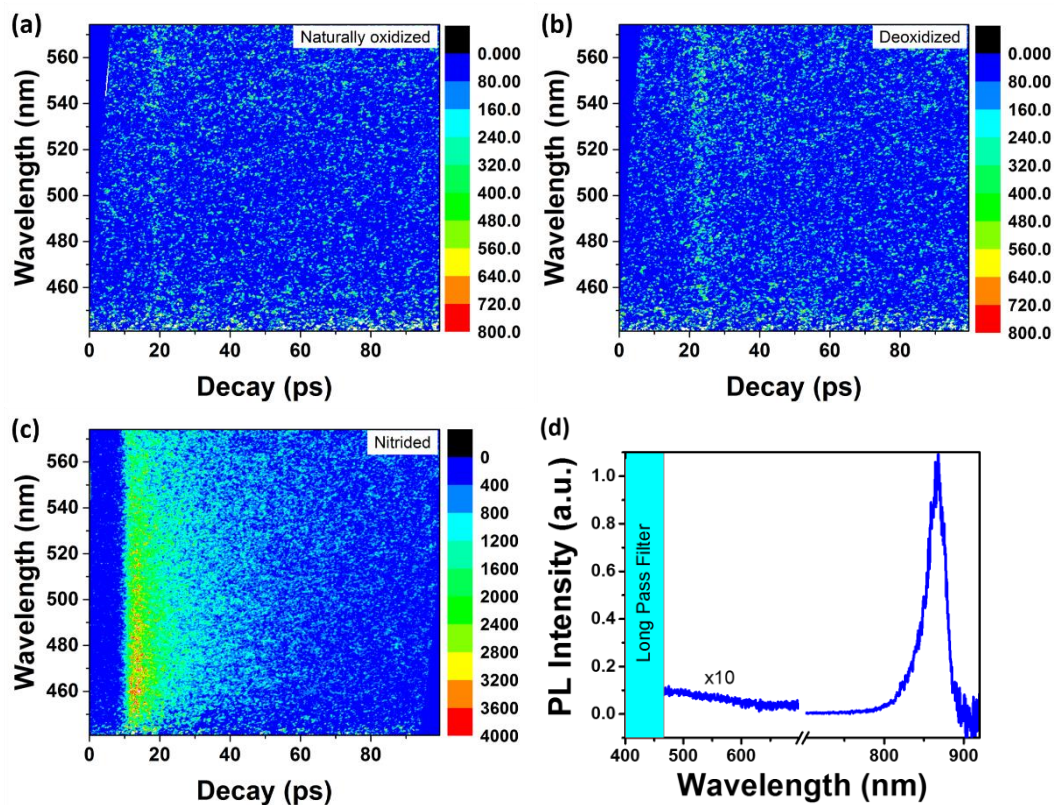
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## S1 PL emissions of naturally oxidized, deoxidized and nitrided GaAs samples at the wavelength from 440 nm to 574 nm

After wet treatments of the nitridation, a  $\text{GaN}_{1-x}\text{As}_x$  layer is formed at the surface of nitrided GaAs. In TRPL measurements, we observe a broad emission band in the range below 600 nm (Figure S1). From Figure S1d we can estimate the maximum of this emission (band gap) to be below 500 nm. This broad band cannot be attributed to the emission of GaAs, which peaks at 870 nm. Instead, this band should come from emission of the  $\text{GaN}_{1-x}\text{As}_x$  layers. According to the References [1,2], the band gap of 500 nm corresponds to the emission of  $\text{GaN}_{1-x}\text{As}_x$  with  $x \sim 0.06$ , which allows us to conclude that the content of As in the surface layer after nitridation is less than 0.06.<sup>1,2</sup>



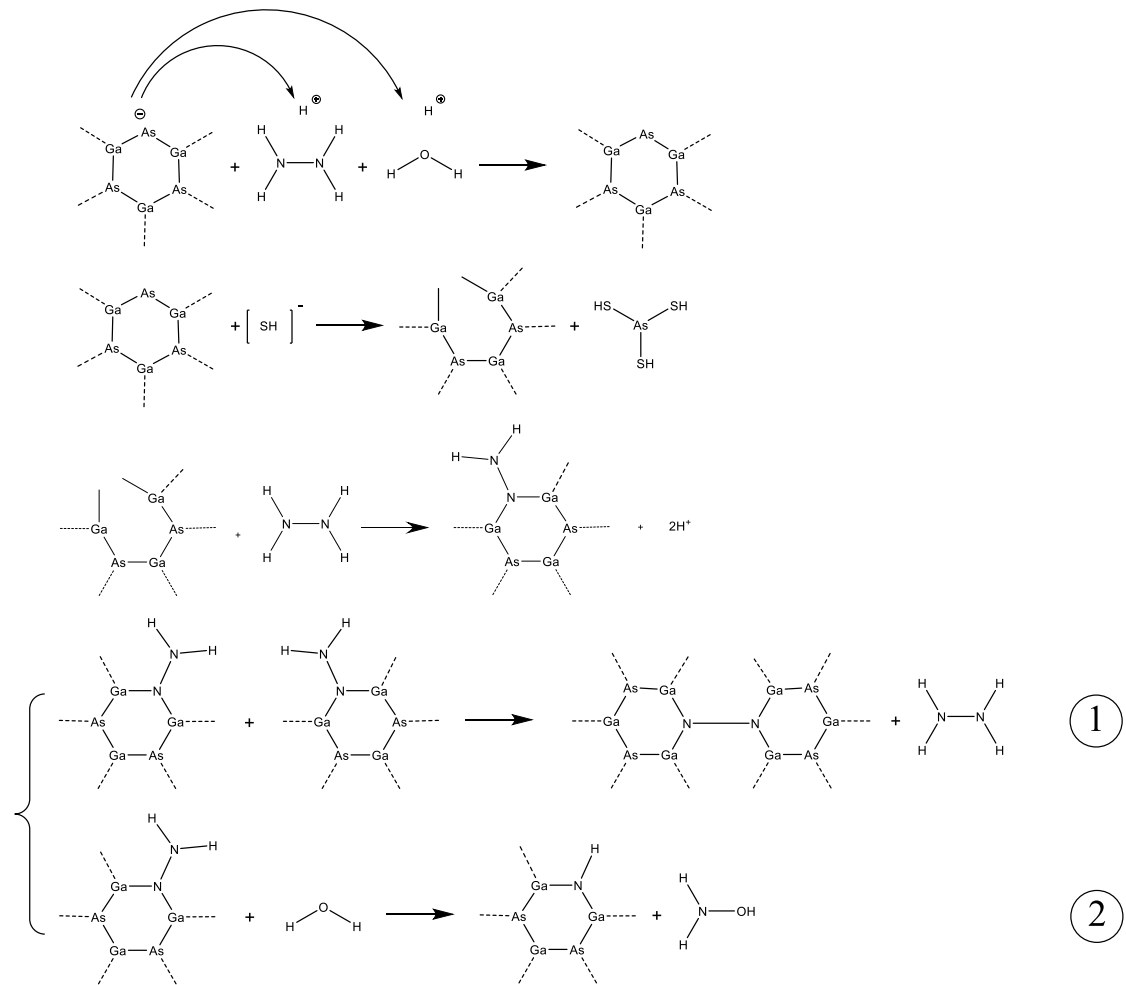
**Figure S1.** Emission of (a) naturally oxidized, (b) deoxidized and (c) nitrided GaAs from 440 nm to 570 nm. PL decays were measured by using excitation at 3.1 eV and collected with a long pass filter transmitting light above 440 nm. (d) Normalized PL intensity of the nitrided GaAs sample.

## S2. Experimental details

### (1) Surface nitridation and deoxidation of GaAs

Naturally oxidized GaAs samples were made of GaAs (100) wafer (Topvondor Technology Co., LTD, intrinsic, vertical temperature gradient freezing method (VGF)) with a thickness of 350  $\mu\text{m}$ , cut into  $3 \times 3$  mm pieces and pre-cleaned by acetone (VWR,  $\geq 99.0\%$ ), ethanol (VWR, ethanol absolute,  $\geq 99.8\%$ ) and DI water to remove possible organic contaminants. As a reference, deoxidized GaAs wafers were prepared and studied in this work. To remove GaAs surface oxide, pre-cleaned GaAs was dipped into a 1 M HCl (Sigma–Aldrich, 37%) solution for 30 s at room temperature and rinsed with DI water before being dried in nitrogen. A hydrophobic surface is obtained with a surface terminated by the chlorine bonds. For surface nitridation, the method described in ref. 1 was used. A low alkaline hydrazine-sulfide solution was prepared by adding anhydrous hydrazine-dihydrochloride (Sigma–Aldrich,  $\geq 99.99\%$ ) into hydrazine-hydrate (Sigma–Aldrich, 40-50%) up to pH~8.5. The solution was heated up to 80 °C after introducing sodium sulfide nonahydrate,  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (Sigma–Aldrich,  $\geq 99.8\%$ ) to the concentration of 0.01 M. Then, the GaAs (100) wafers were immersed into this solution for 3, 6, 10, 15, 25, 40, 60 mins. After that, the samples were rinsed by deionized water and then dried in nitrogen. After nitridation, a thin  $\text{GaN}_{1-x}\text{As}_x$  layer at the GaAs surface should be formed. The details of the nitridation reaction processes are shown in Scheme S1: Reaction 1, HCl in the alkaline hydrazine sulfide solution removes the native oxide, such as  $\text{Ga}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$ , and forms dangling bonds. Then, the dangling bonds are vanished at the GaAs surface via electron transfer process from GaAs to  $(\text{N}_2\text{H}_5)^+$  or  $(\text{H}_3\text{O})^+$ . Reaction 2, a Ga-terminated surface is formed by dissolving As atoms by the reaction with  $\text{SH}^-$  in solution. Reaction 3, the surface terminates by

hydrazine molecules. Reaction 4, a GaN layer is formed at the surface via the interaction between two N dangling bonds (①) or the reaction between N dangling bond and H<sub>2</sub>O (②). All of the above sample processing was performed in a nitrogen atmosphere.



**Scheme S1.** The schemes of chemical deoxidation and nitridation reaction of GaAs wafer.

## (2) Time-resolved Photoluminescence (TRPL) measurement

The PL decay was measured with the experiment setup described below. The output of a Ti:Sapphire laser (Spectra-Physics, Tsunami) with 100 fs pulse at 770 nm and with

repetition rate of 81 MHz was used for excitation. The excitation light was focused on the GaAs samples at an angle of  $70^\circ$  (close to the Brewster angle for GaAs). By a pair of 1 in. quartz plano-convex lenses of 50 mm focal length, PL was collected nearly perpendicular to the GaAs surface plane and focused on the input slit of the spectrograph (Chromex) with 50 lines/mm grating, blazed at 600 nm (2.07 eV). The output of the spectrograph was imaged onto the input slit of the streak camera (Hamamatsu C6860) set at 20  $\mu\text{m}$ . After background subtraction, shading and spectral sensitivity corrections of the measured PL images were performed with the help of the calibrated reference light source (Ocean Optics, LS-1- CAL). All GaAs were kept in dry  $\text{N}_2$  atmosphere and were measured at room temperature. Efforts were taken to keep the alignment of the experimental set-up the same for all the samples studied. Note that, in order to quantify the PL decay time of the samples, we consider the time obtained via a two-exponential fitting or measured the time when the emission intensity decays to  $1/e$  of its initial value. <sup>3</sup>

### (3) Time-resolved Terahertz Spectroscopy (TRTS) measurement

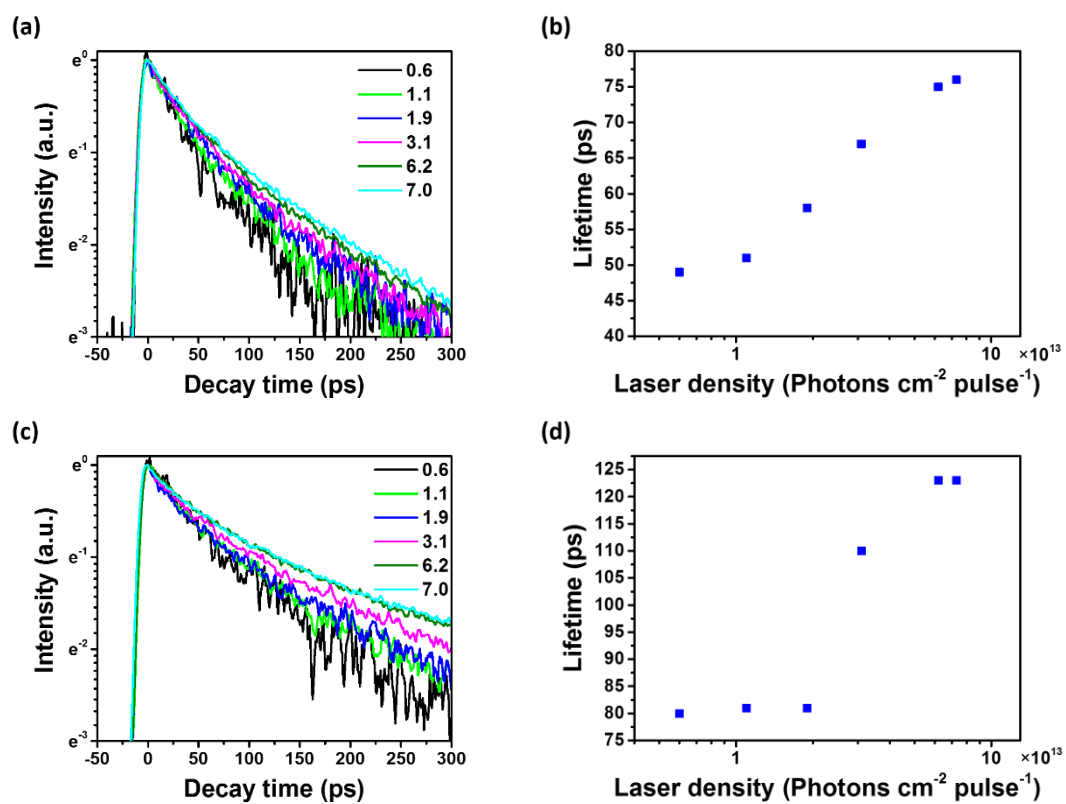
A regenerative amplifier (Spitfire Pro XP, Spectra Physics) seeded by a femtosecond oscillator (MaiTai, Spectra Physics) is used for generating 7 mJ 80 fs laser pulses at 796 nm and 1 kHz repetition rate. The laser beam was split into three: one beam (400  $\mu\text{J}/\text{pulse}$ ) was used to generate THz radiation by optical rectification in a  $\text{MgO}:\text{LiNbO}_3$  crystal; the second beam was used for electro-optical sampling of the THz pulses in a (110)  $\text{ZnTe}$  crystal; the third beam was converted into the second harmonic (398 nm) in a BBO crystal and used for excitation of studied samples. The setup was purged with dry nitrogen to reduce the attenuation of the THz radiation due to water vapor

absorption. Efforts were taken to keep the alignment of the experimental set-up the same for all the samples studied.

#### (4) Absolute quantum yield (PL QY) measurement

A CW laser (780 nm) was used for excitation of the samples placed inside an integrating sphere (HORIBA, Quanta- $\phi$ , F3029), filled by nitrogen. The incident and not absorbed excitation and PL were measured by the spectrometer (AvaSpec-ULS2048-USB2-UA-50). All the spectra were corrected with the help of the calibrated reference light source (Ocean Optics, LS-1-CAL). By taking into account the PL out-coupling and self-absorption effects of the GaAs wafer, the absolute QYs were corrected by multiplying the originally measured value by the same factor of 50 for all samples.<sup>4,5</sup>

**S3 TRPL kinetics and PL decay times of naturally oxidized and deoxidized GaAs under varied excitation photon flux**



**Figure S2.** Normalized TRPL kinetics and PL decay time of GaAs with naturally oxidized (a, b) and deoxidized (c, d) surfaces under varied excitation fluencies from 0.6 to  $7.0 \times 10^{13}$  photons  $\times \text{cm}^{-2}$  pulse $^{-1}$  after photoexcitation at 1.6 eV, respectively.

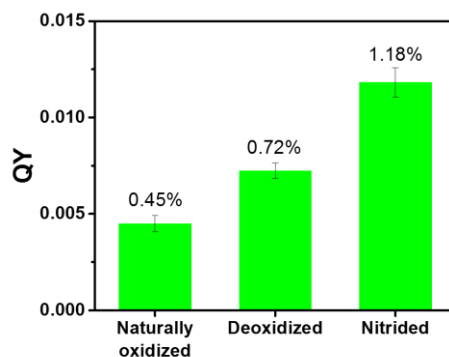
#### S4 Double exponential fitting parameters in Figure 3c

**Table S1.** Double exponential fitting parameters of TRPL kinetics traces in Figure 3c.

Sample	Amplitude $A_1$	Lifetime $\tau_1$ (ps)	Amplitude $A_2$	Lifetime $\tau_2$ (ps)
Naturally oxidation	0.64	44.7	0.31	134.7
Deoxidation	0.46	45.1	0.46	185.6
Nitridation (10 mins)	0.40	45.2	0.55	250.0

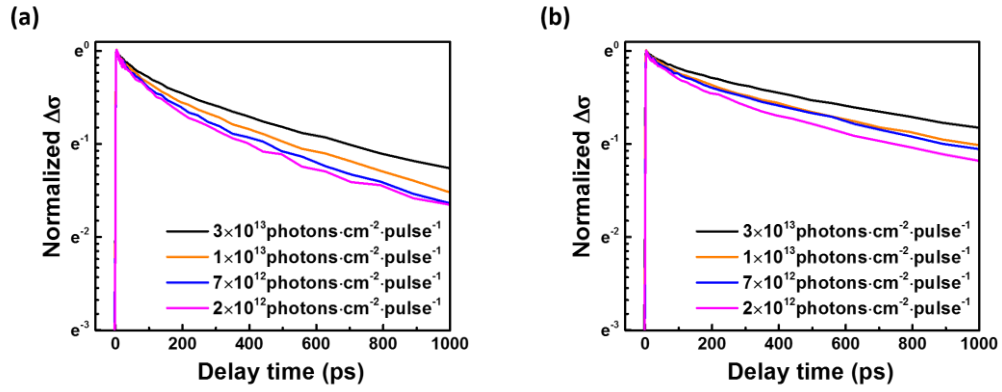


**S5 Absolute PLQY results of naturally oxidized, deoxidized and after 10 min nitridation treated GaAs**



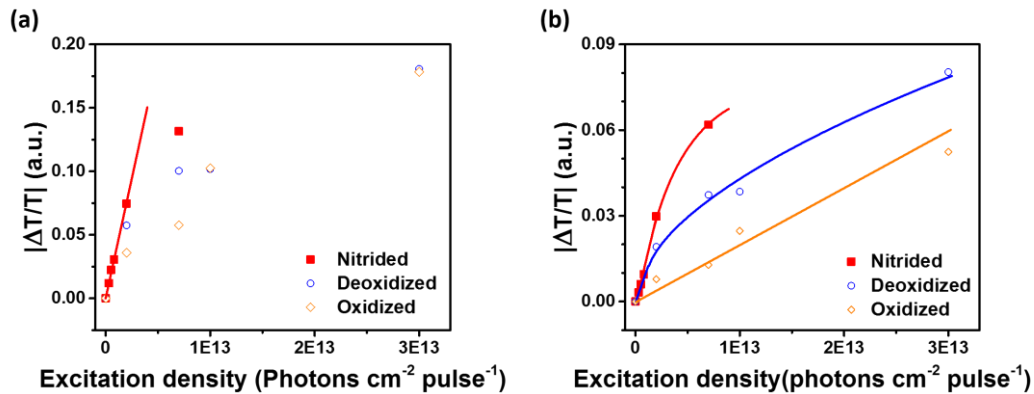
**Figure S3.** Absolute PL QY of GaAs wafers with naturally oxidized, deoxidized and after 10 min nitridation treatment under photoexcitation at 1.6 eV. QY of the GaAs after nitridation is ~2.6 times higher than that of naturally oxidized GaAs and ~1.6 times higher than of the deoxidized GaAs. The excitation intensity was  $1.8 \times 10^{21}$  photons  $s^{-1} cm^{-2}$ .

**S6 TRTS kinetics of naturally oxidized and deoxidized GaAs under varied excitation fluence**



**Figure S4.** Normalized photoconductivity kinetics of (a) naturally oxide and (b) deoxidized GaAs under varied excitation fluencies after photoexcitation at 1.6 eV.

## S7 Photoconductivity at varied excitation fluencies



**Figure S5.** Photoconductivity of GaAs with 10 min nitridation, deoxidized and naturally oxidized measured after photoexcitation at 1.6 eV under varied excitation fluencies at (a) ~ 1 ps delay time and (b) ~1 ns delay time.

Figure S5a shows the excitation density dependence of the TRTS signal, which is proportional to  $\Delta\sigma(t)$  at the early delay time of 1 ps. The signal measured over the first four points in the nitrided sample can be fitted by a linear function. At early delays, we can neglect charge recombination and consider that the concentration of photo-generated charge carriers,  $n$ , is proportional to the excitation density. As  $\Delta\sigma(t) = n(t)q\mu(t)$ , from the fit we can obtain the slope, which is proportional to the electron mobility,  $\mu$ . Figure S5b presents a similar excitation dependency of the TRTS signal measured at 1 ns delay time. The first four points can be well fitted by a linear function. The slope of the signal obtained from the fit is increased by ~30% compared to the 1 ps delay case. Assuming that the slope is still proportional to the electron mobility,  $\mu$ , we have to conclude that mobility has increased with time after excitation, which is not a very likely result. If, on the contrary, we assume that mobility does not change with time, the observed increase of the slope can be associated with the decrease of the recombination rate at higher excitation density. This is an improbable effect as typically recombination should speed up with a concentration of photo-generated charges and

therefore with the excitation density. Yet another reason for seemingly increased density of charges at 1 ns could be correlated with a saturation of the electron trapping effect. Under such a saturation, we expect a larger concentration of mobile electrons at long delay time under higher excitations, which would agree with our observation.

It is interesting to compare the excitation density dependencies observed for other GaAs samples. The difference between the studied samples is expected only at the surface of GaAs. Thus the density of absorbed excitation photons should be the same in all samples. Furthermore, the mobility of electrons in GaAs away from the surface should also be the same in all samples. The fact that for deoxidized and oxidized samples the slope of  $\Delta T/T$  is lower and much lower than in nitride GaAs suggests that electron trapping is much less present in nitride GaAs.

## S8 Double exponential fitting parameters in Figure 4b

**Table S2.** Double exponential fitting parameters of the TRTS decay shown in Figure 4b.

<b>Sample</b>	<b>Amplitude <math>A_1</math></b>	<b>Lifetime <math>\tau_1</math> (ps)</b>	<b>Amplitude <math>A_2</math></b>	<b>Lifetime <math>\tau_2</math> (ps)</b>
Naturally oxidation	0.27	50	0.60	418
Deoxidation	0.23	74	0.61	746
Nitridation (10 mins)	0.19	72	0.81	1312

## S9 Double exponential fitting parameters in Figure 6

**Table S3.** The parameters obtained by two-exponential fitting of the TRPL and TRTS kinetics shown in Figure 6.

Sample	Amplitude $A_1$	Lifetime $\tau_1$ (ps)	Amplitude $A_2$	Lifetime $\tau_2$ (ps)
TRPL_Naturally oxidation	0.56	32	0.59	137
TRPL_Nitridation (10 mins)	0.43	60	0.58	400
TRTS_Naturally oxidation	0.27	50	0.60	418
TRTS_Nitridation (10 mins)	0.19	72	0.81	1312

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