# Optical metastability of subband gap (2.2 eV) yellow luminescence in GaN

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Optical metastability has been studied in undoped GaN films grown on SiC substrates having a previously deposited AlN buffer layer. Brief exposures to a higher intensity ultraviolet light resulted in temporary changes in the optical properties of the GaN layer. The photoinduced changes created high contrast patterns on samples that could be observed under an optical microscope with lower intensity ultraviolet excitation. The subband gap yellow photoluminescence peak at 2.2 eV increased significantly after the patterns were created. This change slowly returned (hours) to its initial value at room temperature. The retention time decreased to a few seconds at temperatures above 100 °C. The data showed that a 1.34 eV thermal activation energy exists, which suggests that the cause of these metastable properties is related to the subband gap yellow luminescence.  [DOI: 10.1063/1.1381417]

GaN and related materials have been extensively studied since the advent of high-brightness blue light emitting diodes.[1] They possess large direct band gaps, strong interatomic bonds, and moderate thermal conductivities, that make them candidates for high temperature/high-power optoelectronic applications.[2,3]

Metastable effects in semiconductor materials can influence optoelectronic device performance via transient changes in emission, absorption, and transport. Optical metastability in bulk GaN single crystals has been observed.[4] Reconfigurable optical properties are also found in InGaN/GaN heterostructures[5] and InGaN/GaN quantum wells grown on sapphire substrates.[6] UV-induced modifications in undoped GaN on sapphire grown by metalorganic chemical vapor deposition (MOCVD) were observed from 9 to 160 K by two different groups.[7,8] Electrical metastability in the form of persistent photoconductivity has also been observed[9,10] in silicon doped *n*-type GaN thin films.

The large band gap and deep levels of GaN make possible metastable effects that are long lived (hours, days) at room temperature compared to smaller band gap semiconductors.[11] Deep levels around 1.2 eV have been found in *n*-type GaN by photoemission capacitance transient spectroscopy,[12] photocapacitance spectroscopy,[13] and surface photovoltage spectroscopy.[14] To date the microscopic origin of these deep levels remains unidentified. Theoretical calculations show that deep levels at about 1.2 eV could be explained by either Ga antisite[15,16] defects or N antisite[17] defects. Mattila *et al.*[17] found that the energy levels for the N antisite varied with different charge states and atomic positions. It was found that both $N_{Ga}^{-1}$ and $N_{Ga}^{-2}$ would result in deep acceptor levels at about 1.2 eV. Saarinen *et al.*[18] found that the concentration of Ga vacancies correlates with the intensity of the yellow luminescence.

In this letter, we report observations of reconfigurable optical properties in undoped GaN films on SiC substrates. Exposure to a high power density UV light increased the peak intensity of the yellow luminescence at 2.2 eV and created high contrast optical patterns on the sample ($77\ K < T < 400\ K$). The peak intensity at 2.2 eV and the contrast of the patterns decreased with time with an activation energy of 1.34 eV.

The epitaxial layers were deposited as follows. The MOCVD reactor is a resistive heated, cold walled quartz system containing a rotating (180 rpm) graphite stage. Trimethylgallium and trimethylaluminum carried in $H_2$ and ammonia were the reactants. Hydrogen was also the diluent gas. A 100-nm-thick AlN buffer layer was deposited on an on-axis 6-H SiC (0001) substrate at 1090 °C (45 Torr). Subsequently a 0.3 $\mu$m GaN layer was deposited at 990 °C (45 Torr).

The frequency tripled output of a pulsed Ti:sapphire laser (250 fs at 76 MHz; 280 nm) was used as the ultraviolet excitation source. Writing images (lines) on the samples was accomplished by focusing the ultraviolet source to a spot size of approximately 20 $\mu$m which produced an average power density of $30\times10^3$ W/cm$^2$. In the "read" condition, the sample was illuminated at $P_{AVE}=0.4$ W/cm$^2$ with the same UV laser source. Additional information regarding the read and "write" conditions can be found in Refs. 5 and 6.

Room temperature photoluminescence (PL) results are shown in Fig. 1. Curve (a) is the PL for the write condition and curve (c) is for the read condition (but not yet written). Curve (b) was taken at an intermediate laser power density. The schematic views of the write and read conditions are shown in Figs. 2(e) and 2(f), respectively. Competition between the band edge and yellow luminescence transitions at

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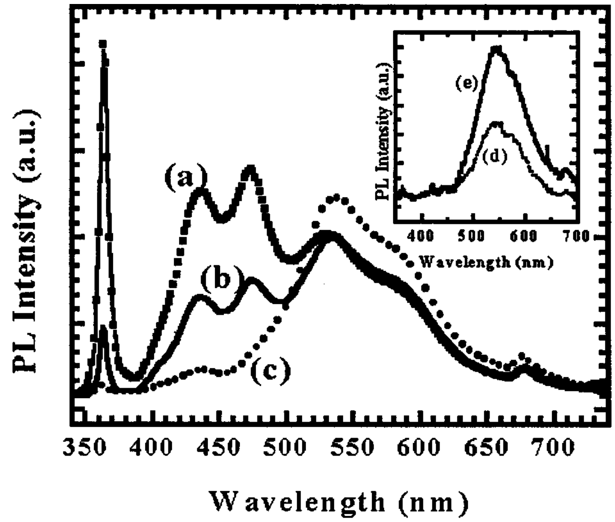


FIG. 1. Room temperature photoluminescence spectra at different power densities. (a) Write condition (30 kW/cm$^2$), (b) intermediate (10 W/cm$^2$), and (c) read condition (0.4 W/cm$^2$). In the inset, curves (d) and (e) are PL spectra under the read condition before and after patterns were created, respectively.

different excitation densities is common in GaN and indicates that deep defect levels are involved.

The appearance of the sample under the microscope under the read condition prior to exposure is shown in Fig. 2(a). The sets of parallel horizontal lines shown in Fig. 2(b) were written at room temperature. No pattern was observed under room lighting or under a high power optical microscope using visible-light illumination. The sample was then stored under room light at room temperature. Photographs 2(c) and 2(d) were taken under the read condition after one and 24 h, respectively. The visible contrast between the pattern and the background diminished with time. After 24 h [Fig. 2(d)], the lines were invisible and were considered erased. It was possible to rewrite the patterns in the same location.

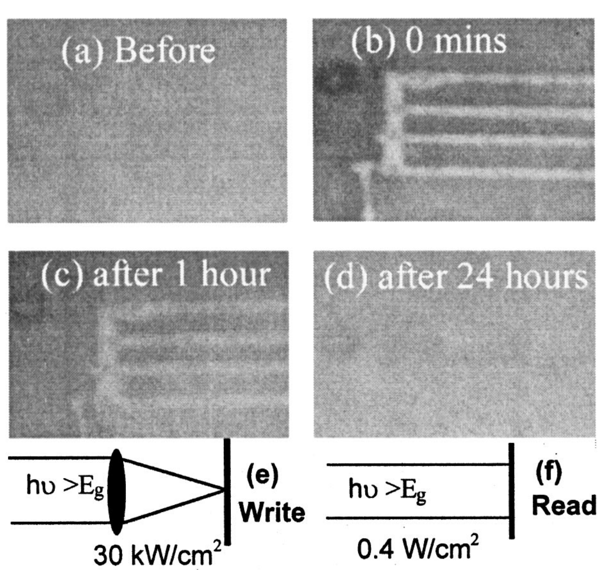


FIG. 2. An optical pattern consisting of a set of parallel lines written on the GaN film by high-intensity UV light (write condition) at room temperature, as shown in (b) and (c). The background color is green and the color of the lines is yellow. The photoinduced pattern is clearly observed in low intensity UV light (read). The pattern slowly disappears with time as shown in (b)–(d).

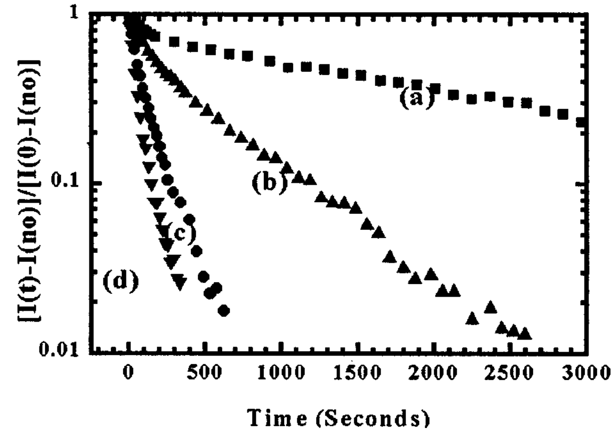


FIG. 3. Decay of the photoluminescence peak intensity at 550 nm after the patterns are created at various temperatures. (a) ■ 35 °C, (b) ▲ 45 °C, (c) ● 50 °C, and (d)▼ 55 °C.

The photoluminescence within the written patterns was investigated by taking spectra under the read condition before and after writing a pattern on the samples. The peak intensity at 550 nm increased significantly after writing (see inset of Fig. 1). The enhanced yellow PL peak was consistent with visual observations. After writing, the yellow peak intensity decreased slowly with time. At room temperature, the peak intensity returned to its initial value and the yellow memory patterns disappeared after about 2 h. At 100 °C, the memory effect disappeared in several seconds. At 130 °C the memory pattern could not be produced under the write condition.

The decay rate of the PL peak at 550 nm was a direct function of temperature, as shown in Fig. 3. The decay of the peak intensity was similar to that reported in the persistent photoconductivity (PPC) studies.[9,10] The decay of the yellow luminescence was also fit to a stretched exponential function[19] of the form $I_{\rm mem}(t)=I_{\rm NO}+(I_0-I_{\rm NO})\times\exp[-(t/\tau)^\beta]$, where $I_{\rm NO}$ is the PL intensity when there is no memory pattern, $I_0$ is the initial yellow peak intensity after writing the pattern, $\tau$ is the time scale of the process, and $\beta$ is the deviation from a single exponential decay and is indicative of the overall structure of whatever system is represented by the stretched exponential relaxation. A summary of the stretched exponential analysis is presented in Table I. The result that $\beta$ is similar throughout the temperature range investigated suggests that the mechanism of the decay is similar as well. In addition, the temperature dependence of $\tau$ can be described as $\tau=\tau_0\exp[\Delta E/kT]$, where $\Delta E$ is the thermal activation energy.

The experimental data for $\tau$ at different temperature and the least square fit to the data is shown in Fig. 4. The resulting thermal activation energy $\Delta E$ is 1.34 eV and

TABLE I. Stretched exponential analysis used to fit the decay of the yellow luminescence.

| Temp. (°C) | $\beta$ | $\tau$ (s) | Correlation |
|---|---|---|---|
| 35 | 0.60587 | 1824.753 | 0.991480 |
| 45 | 0.66372 | 382.189 | 0.994652 |
| 50 | 0.76306 | 90.349 | 0.995469 |
| 55 | 0.61504 | 69.527 | 0.971633 |
| 60 | 0.75029 | 49.904 | 0.979249 |

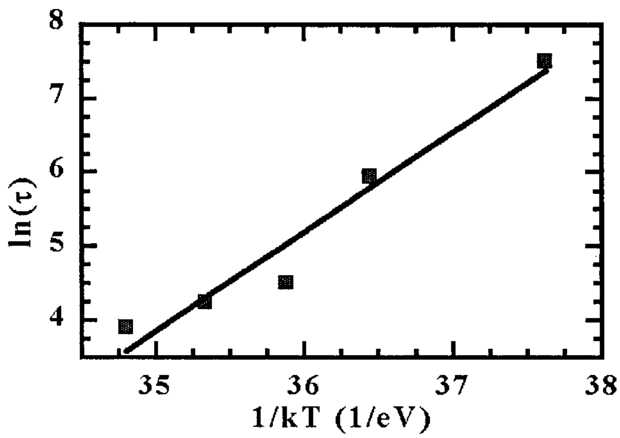


FIG. 4. Experimental data points (square blocks) and fitted curve (solid line) according to a stretched exponential equation. The extracted thermal activation energy is 1.34 eV. Note that $E_g \approx h\nu_{\text{yello}} + \Delta E_{\text{activation}}$.

$\ln(\tau_0) = -40.475$. The small values of $\tau$ at high temperature are consistent with the visual observations described earlier. Note that the difference between the bandgap of the GaN and the fitted 1.34 eV thermal activation energy is about 2.06 eV, which is in the range for the so-called "yellow" luminescence $E_g \approx h\nu_{\text{yellow}} + \Delta E_{\text{activation}}$.

We suggest that the effect of intense laser illumination is to influence the number of, or the charge state, of one or more of these deep levels at approximately 1.2 eV. This results in the increased intensity of the yellow luminescence and the yellow memory effect pattern observed on the sample under low intensity ultraviolet illumination. The yellow luminescence (and the observable patterns) fades with time (and temperature) and returns to the original condition.

In conclusion, the ability to write, store, and read information with ultraviolet light on an undoped GaN layer on a SiC substrate has been demonstrated. Intense laser light caused the subband gap peak intensity at 550 nm to increase significantly and produce a yellow pattern when viewed under low power ultraviolet illumination. The yellow peak slowly decreased with increasing time or temperature with a thermal activation energy of 1.34 eV. The difference between the band gap of GaN and the thermal activation energy suggests that this memory effect is related to the yellow luminescence that is commonly seen in GaN materials. Furthermore, a similar approach of using stretch exponential analysis to PPC in GaN suggests that these two phenomena may have the same angle.

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