Electroluminescence at GaN and $Ga_xIn_{1-x}N$
Electrodes in Aqueous Electrolytes

**Chen-Jen Hung,[a] Lara I. Halaoui,[a] Allen J. Bard,[a,*,z] Paul A. Grudowski,[b]
Russell D. Dupuis,[b,*] Jay Molstad,[c] and Francis J. DiSalvo[c]**

[a]*Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA*
[b]*Microelectronics Research Center, The University of Texas at Austin, Austin, Texas 78712, USA*
[c]*Department of Chemistry, Cornell University, Ithaca, New York 14853, USA*

Electroluminescence (EL) of single crystal and thin films of GaN and $Ga_xIn_{1-x}N$ ($x = 0.8$) was observed in aqueous solution containing peroxydisulfate on passage of cathodic currents. The resulting emission was compared with the photoluminescence of the same materials on ultraviolet light excitation. Only the subbandgap emission was observed in EL for GaN electrodes. The position and intensity of this emission peak depended on the applied potential, with a significant blue shift observed with increasing applied potential. The EL spectra of $Ga_xIn_{1-x}N$ only showed a yellow luminescence band at lower applied potentials. When a more negative potential was applied, the near-bandedge emission (2.9 eV) appeared.
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The III-V nitride semiconductors and their ternary compounds have recently attracted significant interest because of their potential use in optoelectronic devices, such as visible and ultraviolet (UV) light emitting diodes (LEDs) and lasers. It was mainly the realization of bright blue and green LEDs based on GaN heterostructures that spurred the increased efforts in making and understanding the properties of these materials.[1] InN, GaN, and AlN are direct bandgap semiconductors with bandgap energies of 1.9, 3.4, and 6.2 eV, respectively. The size of the bandgap can be manipulated, with energies ranging from the red region in the visible to the deep UV region, by varying the composition of the ternary materials.[2] While the optical characterization of these compounds by photoluminescence (PL) and solid-state electroluminescence (EL) has been extensively investigated, no reports of solution phase EL have appeared. Light can be generated at semiconductor electrodes through electron-hole recombination by the use of specific electrode reactions. The principles of this experiment are shown in Fig. 1. In this article, we report the EL properties of single crystal n-type GaN and $Ga_xIn_{1-x}N$ thin films and bulk single crystal electrodes in the presence of peroxydisulfate.

Experimental

The GaN and $Ga_xIn_{1-x}N$ ($x = 0.8$) thin film electrodes in this study were grown by low-pressure metallorganic chemical vapor deposition (MOCVD) on sapphire substrates.[3,4] The primary precursors employed were trimethylgallium (TMGa), trimethylindium (TMIn), ammonia (NH_3), and silane (SiH_4) for the n-type doping. The Si-doped GaN thin film was 1.5 μm thick and the $Ga_xIn_{1-x}N$ thin film was 200 nm thick on a 1.5 μm thick GaN layer. Bulk single crystals of GaN were synthesized by heating NaN_3 and Ga metal in a stainless steel tube sealed under nitrogen atmosphere at 600-800°C for 24-96 h.[5] Larger single crystals, with dimensions > 0.1 mm, were prepared at 700-800°C with 3 mmole of NaN_3.[5] GaN single crystal electrodes (0.6-0.7 mm) were used for this study. These electrodes were etched in 1 M KOH at 70°C for 25 s before a series of measurements. Ohmic contact to films and crystals was made with Ga-In eutectic; the contact was shielded from the solution with epoxy cement. The EL experiments employed a conventional three-electrode configuration in a quartz cell containing a platinum gauze electrode as the auxiliary electrode and a Ag/AgCl electrode as the reference electrode. The luminescence was obtained by applying a constant potential to the semiconductor working electrode in an aqueous 0.1 M $K_2S_2O_8$ solution. A charge-coupled device (CCD) camera (model AT200, Photometrics, Phoenix, AZ) cooled to -134°C was
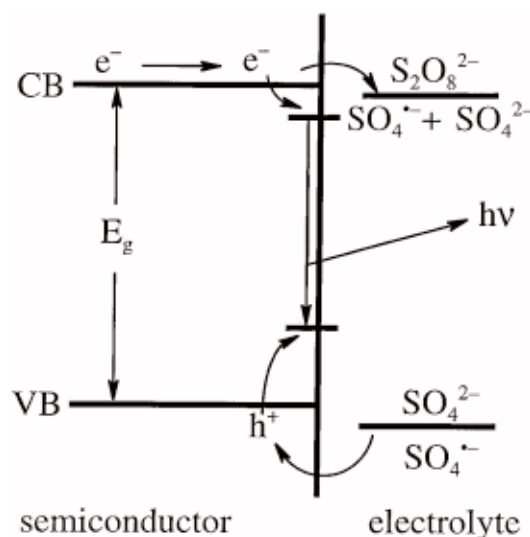
Figure 1. Schematic diagram of the electrode reactions.

used to acquire EL spectra. The PL measurements were performed at room temperature with excitation by a continuous-wave argon-ion laser operating at a wavelength of 275.4 nm. A GaAs-photocathode photomultiplier tube was used as the detector and a digital electrometer was used for measuring the detector current.

Results and Discussion

The EL observed during reduction of peroxydisulfate has been studied at various materials.[6,7] The luminescence produced by recombination of an electron with a hole in the semiconductor has been attributed to a two-step reduction mechanism of peroxydisulfate (Fig. 1).[6-8] The initial step (Eq. 1) occurs by electron transfer from the conduction band (CB) to $S_2O_8^{2-}$
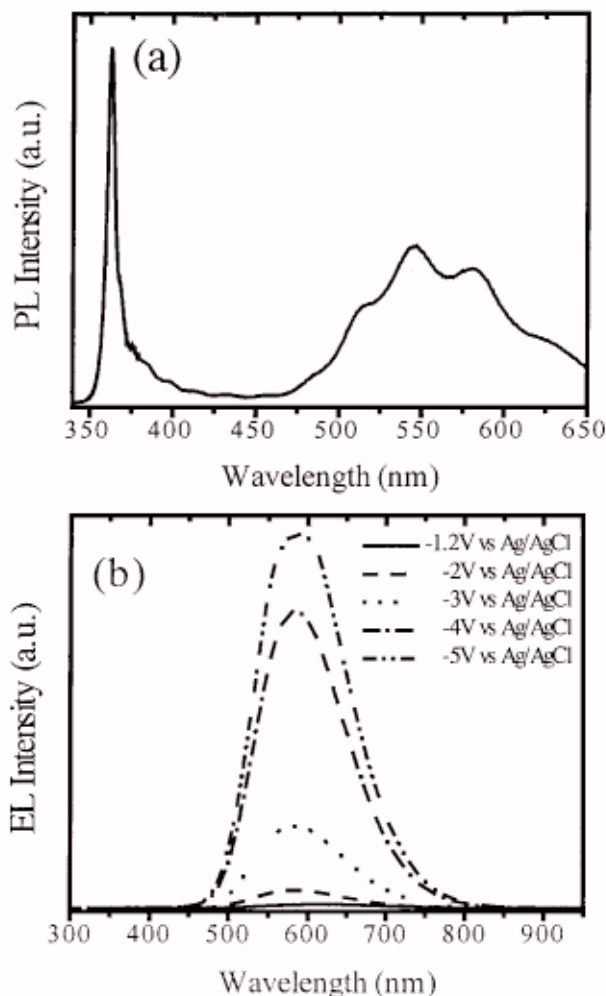
$$S_2O_8^{2-} + e^- \text{ (CB)} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \qquad \varepsilon^o \leq 0.6 \text{ V vs. NHE} \qquad [1]$$

The oxidizing strength of $SO_4^{\bullet-}$ is sufficient to capture an electron from the valence band (VB) and thus cause injection of a hole into the valence band in the second step

$$SO_4^{\bullet-} \rightarrow SO_4^{2-} + h^+ \text{ (VB)} \qquad \varepsilon^o \geq 3.4 \text{ V vs. NHE} \qquad [2]$$

The PL spectrum of a Si-doped GaN sample at room temperature is

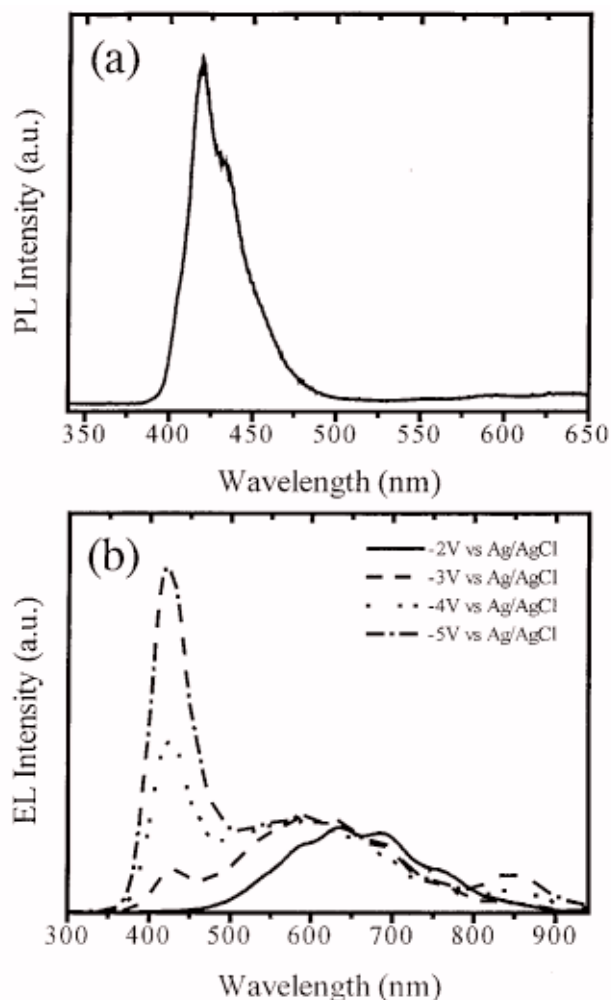* Electrochemical Society Fellow.
z E-mail: ajbard@mail.utexas.edu

Figure 2. (a) Room-temperature PL of Si-doped GaN thin film. The near-bandedge and the yellow transition occur at 363 and 575 nm, respectively. (b) EL spectra at different step potentials on the same thin film GaN electrode in 0.1 M $K_2S_2O_8$ at pH 2.7.

Figure 3. (a) Room-temperature PL of $Ga_xIn_{1-x}N$ thin film. The near-bandedge emission occurs at 420 nm. (b) Development of EL spectra for different potential pulses on the same thin film $Ga_xIn_{1-x}N$ electrode in 0.1 M $K_2S_2O_2$ at pH 2.7.

shown in Fig. 2a. The near-bandedge and the yellow transition are centered around 363 and 575 nm, respectively. Figure 2b shows EL spectra at different step potentials on the same thin film GaN electrode in 0.1 M $K_2S_2O_8$ at pH 2.7. The radiative recombination of the injected holes with conduction band electrons did not produce near-bandedge emission. The subbandgap emission observed in both PL and EL has been attributed to transitions to deep acceptor levels, probably due to the gallium vacancies.[9] The EL spectra were blue shifted by about 32 nm in λ_{max} with the applied potential changing from -1.2 to -5 V vs. Ag/AgCl. The intensity of the EL also increased with increasing negative applied potential. The blue shift of the emission peak with increasing excitation rate has also been observed with several II-VI semiconductors like ZnS.[7]

The photogeneration rate of excess carriers with greater than bandgap optical excitation conditions employed for the PL data are probably much higher than the corresponding e-h pair generation under EL conditions. We would normally expect that such trap-related luminescence would be saturated at relatively high excitation levels with bandedge recombination making a strong contribution relative to the trap luminescence under high-intensity excitation. However, at low excitation intensities, the traps capture virtually all of the excess carriers and the trap-related luminescence dominates in the EL spectrum.

The room-temperature PL spectrum of a $Ga_xIn_{1-x}N$ sample is shown in Fig. 3a. The spectrum shows a strong near-bandedge emis-

sion at 420 nm and a broad subband emission in the lower energy region. Figure 3b shows the EL spectra for steps to different potentials on the same thin film $Ga_xIn_{1-x}N$ electrode in 0.1 M $K_2S_2O_8$ at pH 2.7. The EL spectrum of a $Ga_xIn_{1-x}N$ electrode showed only the yellow luminescence band at an applied potential of -2 V vs. Ag/AgCl. When a more negative potential was applied, the intermediate states that are filled from the conduction band became saturated and the near-bandedge emission (2.9 eV) was more prominent. Comparison of the PL spectrum and the EL spectra shows a more pronounced yellow band transition for the EL measurements. The small periodic intensity modulation within the yellow band (500-900 nm), e.g., shown in the -2 V curve (solid line) in Fig. 3b, can be attributed to interference effects in the ~200 nm thick $Ga_xIn_{1-x}N$ layer.[10]

The EL spectra of bulk single crystal GaN with the potential pulse of -1 and -2 V vs. Ag/AgCl are shown in Fig. 4. A broad emission peak at 620 nm was observed with a potential step to -1 V, this shifted to 580 nm when a potential of -2 V was applied, consistent with the trend observed for the GaN thin films. Because of the small size of the crystal (exposed area ≈ 0.6 mm²), hydrogen gas, which is evolved with all of these electrodes at these negative potentials, built up and covered the entire single crystal surface, resulting in a decrease of the light intensity with time. This effect became more important at more negative potentials (higher currents) and accounts for the observed decrease in emission at -2 V (Fig. 4) and prevented
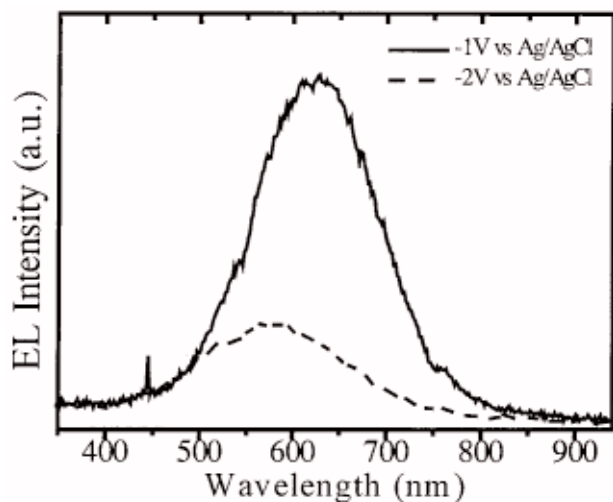
Figure 4. EL spectra of bulk single crystal GaN for different potential pulses.

measurements at more negative potentials. However, the light emission could be restored if hydrogen was removed by bubbling nitrogen past the electrode.

Conclusion

We have demonstrated that EL can be generated in single crystal GaN and $Ga_xIn_{1-x}N$ thin films, as well as bulk single crystal GaN electrodes in aqueous solution. Compared with PL, the EL of both GaN and $Ga_xIn_{1-x}N$ electrodes exhibited stronger yellow band emissions.

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