

Microsensors Based on GaN Semiconductors Covalently Functionalized with Luminescent Ru(II) Complexes

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Development of integrated devices for chemical monitoring is a priority goal of very different areas such as lab-on-a-chip systems, portable environmental monitors, cell-phone-as-sensor devices, and medical sensors, to name a few, where the device size and fast response are paramount. With the development of a thermal annealing method for mass production of gallium nitride, Nakamura marked the onset of a new era of solid-state blue/violet/UV light-emitting diodes (LEDs).¹ Nitride semiconductors have outstanding physical, electronic, and optoelectronic properties, such as their physical hardness, chemical stability, high electron mobility, presence of piezoelectric fields, and direct band gap, allowing their use in various applications such as power electronics, data storage, and lighting.² Surface functionalization of GaN with adequate luminescent molecular probes would enable integrated microcircuits with chemical sensing features. With this aim in mind, we selected O₂ sensing to prove the feasibility of such a concept. Luminescent Ru(II) polyazaheterocyclic complexes reign among all blue-absorbing O₂ indicator dyes because of their >150 nm Stokes shifts, 0.2–8 μs lifetimes, and high photostability and the nearly diffusion-limited rate of quenching of their metal-to-ligand charge transfer (MLCT) excited state with O₂.³

In this work, covalent tethering of a Ru(II) dye to GaN surfaces has been accomplished as a key step in the development of innovative sensing devices in which the indicator support (semiconductor) plays the role of both support and excitation source. Some reports of GaN functionalization have been published to date; these involve just surface adsorption⁴ or more stable covalent bonding,⁵ but to the best of our knowledge, no molecular dye has been chemically immobilized on the surface to take advantage of the emitting properties of this semiconductor.

A functionalization sequence based on n-GaN surface oxidation, silanization with 3-aminopropyltriethoxysilane (APTES), and final reaction with the sulfonyl chloride of the luminescent complex tris[(1,10-phenanthroline-4,7-diyl)bis(benzenesulfonate)]-ruthenate(4-), [Ru(pbbs)₃]⁴⁻, leads to the desired covalent attachment of the O₂ indicator dye via formation of a strong sulfonamide bond (for further details, see the Supporting Information). Details of the GaN sample growth, oxidation, and silanization steps have been reported elsewhere.^{5a} Luminescence lifetime decays of the initial and thoroughly washed derivatized GaN surfaces were recorded with a confocal fluorescence lifetime imaging microscope (FLIM, Horiba) to confirm the presence of the Ru(II) dye on the surface (Figure 1). No significant emission could be observed for either pure or silanized GaN surfaces,

while a long-lived strong emission was recorded for the Ru(pbbs)₃-functionalized surface.

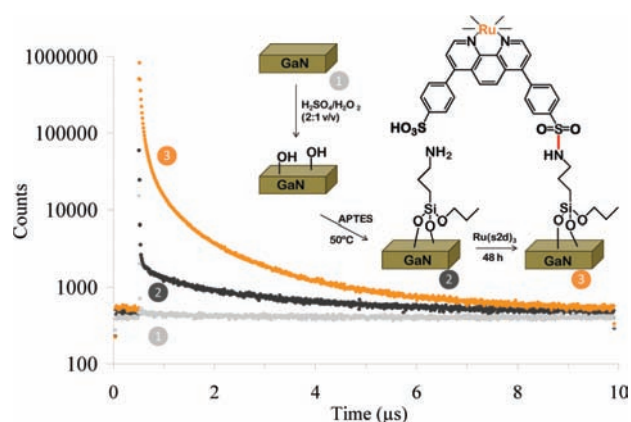


Figure 1. Luminescence decays of the initial (light gray), silanized (dark gray), and Ru(pbbs)₃-functionalized (orange) GaN surfaces ($\lambda_{exc} = 470$ nm; $\lambda_{em} > 590$ nm). Possible causes of decay 2 are discussed in the Supporting Information.

Emission decays from the photoexcited Ru(pbbs)₃ were successfully fitted without deconvolution to a sum of three exponentials. However, more than just three microenvironments are expected to exist around the luminescent probe, depending on the proximity of nearby complexes and/or the number of bonds between each complex and the surface (see below).

Although the chosen GaN was n-type, the surface of which was completely covered by a dense three-silane-layer film,^{5a} the attached dye concentration did not allow recording of a steady-state luminescence spectrum. Nevertheless, a time-resolved emission spectrum (TRES) of the immobilized dye (for further details, see the Supporting Information) revealed an emission band between 550 and 750 nm with a maximum at 620 ± 10 nm that matches the MLCT band of Ru(pbbs)₃.⁶

Once the presence of the dye on the surface was confirmed, the next step was to determine whether the dye had just been adsorbed on the surface or a covalent bond had formed between the dye and the aminosilylated GaN surface. To this end, a second semiconductor sample containing [Ru(pbbs)₃]⁴⁻ adsorbed over a silanized GaN surface was prepared. Figure 2 shows the S 2p core-level spectra measured using X-ray photoelectron spectroscopy (XPS) for the adsorbed and expected covalently bound Ru complexes after background subtraction with a modified Shirley method.⁷

The S 2p core-level spectra shown in Figure 2 are located at 168–169 eV and do not overlap with the Ga 3s core-level spectrum

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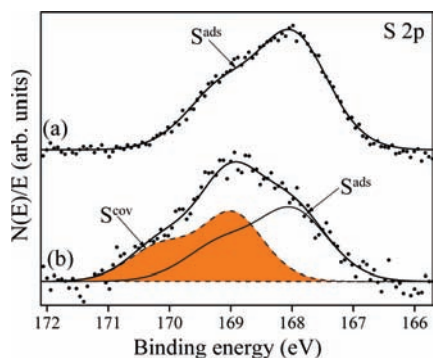


Figure 2. S 2p core-level XPS spectra (dots) and fitted functions for (a) adsorbed (solid line) and (b) covalently bound (dashed line) $[\text{Ru}(\text{pbbs})_3]^{4-}$ on silanized GaN substrates.

of the GaN substrate at ~ 161 eV. The experimental spectrum of the adsorbed Ru compound (S^{ads} , Figure 2a) can be reproduced by a double peak with the main S $2p_{3/2}$ component at 168.0 eV, a spin-orbit splitting of 1.2 eV, a full width at half-maximum (fwhm) of 1.4 eV for each of the doublet components, and a theoretical S $2p_{3/2}/2p_{1/2}$ area ratio of 2. Moreover, the spin-orbit splitting used to reproduce the experimental spectrum is in good agreement with the literature values for the S 2p doublet in several S-containing groups,⁸ and the observed binding energy agrees with that previously reported for sulfonate species.⁹ Therefore, the S^{ads} spectrum can be used as a reference of noncovalently bound Ru sulfonate species.

After functionalization of the GaN surface with the Ru complex (Figure 2b), the XPS spectrum broadens and the maximum shifts to higher binding energies, suggesting that in addition to sulfonate groups, other sulfur species appear. In this case, to reproduce the experimental spectrum, it was necessary to introduce not only the S 2p band associated with sulfonate species (S^{ads} , solid line), but an additional S 2p band at higher binding energies (S^{cov}) that had to be assigned to the new *sulfonamide* group (dashed line and shaded area). This new S 2p band, shifted 1 eV to higher binding energy, could also be reproduced by a double peak with the main S $2p_{3/2}$ component at 169.0 eV, a spin-orbit splitting of 1.2 eV, a fwhm of 1.2 eV for each of the doublet components, and a theoretical S $2p_{3/2}/2p_{1/2}$ area ratio of 2. The deconvolution of the S 2p core-level spectrum with the two S species mentioned above yielded a $S^{\text{ads}}/S^{\text{cov}}$ ratio of 1.2, suggesting that two to three of the six sulfonate groups of the Ru indicator dye are involved in the covalent bonding. Additionally, this low ratio is evidence that the dye was covalently bound and not just adsorbed on the surface, since large amounts of adsorbed complex would lead to much higher $S^{\text{ads}}/S^{\text{cov}}$ ratios.

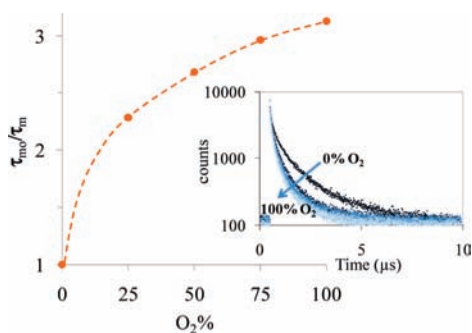


Figure 3. Stern–Volmer plot for the O_2 quenching of photoexcited $\text{Ru}(\text{pbbs})_3$ covalently bound to the GaN surface ($\tau_m = \sum B_i \tau_i / \sum B_i$).

The final step was determining the extent to which the chemical attachment affected the O_2 sensing properties of the indicator dye. The Stern–Volmer (SV) plot for the quenching of GaN surface-bound $\text{Ru}(\text{pbbs})_3$ is shown in Figure 3. The pre-exponentially weighted emission lifetime (τ_m) decreased from ~ 650 ns under N_2 to 200 ns under O_2 . The nonlinearity of the SV plot is attributed to the existence of microdomains on the surface.¹⁰ The O_2 sensitivity of the new device is comparable to those of other ruthenium complex-based sensors (polydimethylsiloxane membranes¹⁰ or crystals¹¹).

In conclusion, a chemically sensitive GaN chip has been prepared for the first time by covalently bonding a luminescent indicator dye to the surface. This achievement paves the way to a new generation of integrable ultracompact microsensors that combine semiconductor emitter–probe assemblies. The use of novel nanostructured GaN materials (wires,¹² columns,¹³ or quantum dots¹⁴) with an extremely large surface should improve the sensing performance. Fabrication of a fully operational LED microsensors based on functionalized GaN substrates is currently under way.

Acknowledgment. The authors thank Dr. David Garcia Fresnadillo for useful scientific discussions. This project was funded by the Madrid Community Government (IV PRICYT, ref CM-S-505/AMB/0374 “Futursen”), the ERDF, the ESF, the Spanish MICINN (CTQ2006-15610-C02-01 and TRA2007-30965-E), and UCM-Santander (GR58-08-910072).

Supporting Information Available: Measurement, equipment, and synthesis details; TRES results; and experiments to obtain the SV plot. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Nakamura, S.; Pearton, S.; Fasol, G. *The Blue Laser Diode: The Complete Story*, 2nd ed.; Springer: Berlin, 2000.
- (2) Piprek, J. *Nitride Semiconductor Devices*; Wiley-VCH: Weinheim, Germany, 2007.
- (3) (a) Demas, J. N.; DeGraff, B. A.; Coleman, P. B. *Anal. Chem.* **1999**, *71*, 793A. (b) Wolfbeis, O. S. In *Optical Sensors: Industrial, Environmental and Diagnostic Applications*; Springer: Berlin, 2004; Vol. 1, pp 1–34. (c) Papkovsky, D. B. *Methods Enzymol.* **2004**, *381*, 715. (d) Orellana, G.; García-Fresnadillo, D. In *Optical Sensors: Industrial, Environmental and Diagnostic Applications*; Springer: Berlin, 2004; Vol. 1, pp 309–357.
- (4) (a) Estéphan, E.; Larroque, C.; Cuisinier, F. J. G.; Bálint, Z.; Gergely, C. *J. Phys. Chem. B* **2008**, *112*, 8799. (b) Chang, C. Y.; Kang, B. S.; Wang, H. T.; Ren, F.; Wang, Y. L.; Pearton, S. J.; Dennis, D. M.; Johnson, J. W.; Rajagopal, P.; Roberts, J. C.; Piner, E. L.; Linthicum, K. J. *Appl. Phys. Lett.* **2008**, *92*, 232102.
- (5) (a) Arranz, A.; Palacio, C.; García-Fresnadillo, D.; Orellana, G.; Navarro, A.; Muñoz, E. *Langmuir* **2008**, *24*, 8667. (b) Baur, B.; Steinhoff, G.; Hernandez, J.; Purrucker, O.; Tanaka, M.; Nickel, B.; Stutzman, M.; Eickhoff, M. *Appl. Phys. Lett.* **2005**, *87*, 263901. (c) Kang, B. S.; Ren, F.; Wang, L.; Lofton, C.; Tan, W. W.; Pearton, S. J.; Dabiran, A.; Osinsky, A.; Chow, P. P. *Appl. Phys. Lett.* **2005**, *87*, 023508. (d) Ganguly, A.; Chen, C.-P.; Lai, Y.-T.; Kuo, C.-C.; Hsu, C.-W.; Chen, K.-H.; Chen, L.-C. *J. Mater. Chem.* **2009**, *19*, 928. (e) Kim, H.; Colavita, P. E.; Metz, K. M.; Nichols, B. M.; Sun, B.; Uhrlich, J.; Wang, X.; Kuech, T. F.; Hamers, R. J. *Langmuir* **2006**, *22*, 8121.
- (6) García-Fresnadillo, D.; Orellana, G. *Helv. Chim. Acta* **2001**, *84*, 2708.
- (7) Proctor, A.; Sherwood, P. M. A. *Anal. Chem.* **1982**, *54*, 13.
- (8) Yakimova, R.; Steinhoff, G.; Petoral, R. M.; Vahlberg, C.; Khranovskyy, V.; Yazdi, G. R.; Uvdal, K.; Spetz, A. L. *Biosens. Bioelectron.* **2007**, *22*, 2780.
- (9) Petoral, R. M.; Yazdi, G. R.; Spetz, A. L.; Yakimova, R.; Uvdal, K. *Appl. Phys. Lett.* **2007**, *90*, 223904.
- (10) López-Gejo, J.; Haigh, D.; Orellana, G. *Langmuir* [Online early access]. DOI: 10.1021/la902546k. Published Online: Aug 28, 2009.
- (11) McGee, K. A.; Mann, K. R. *J. Am. Chem. Soc.* **2009**, *131*, 1896.
- (12) Chen, C.-C.; Yeh, C.-C.; Chen, C.-H.; Yu, M.-Y.; Liu, H.-L.; Wu, J.-J.; Chen, K.-H.; Chen, L.-C.; Peng, J.-Y.; Chen, Y.-F. *J. Am. Chem. Soc.* **2001**, *123*, 2791.
- (13) Calleja, E.; Sánchez-García, M. A.; Sánchez, F. J.; Calle, F.; Naranjo, F. B.; Muñoz, E.; Jahn, U.; Ploog, K. H. *Phys. Rev. B* **2000**, *62*, 16826.
- (14) Weidemann, O.; Kandaswamy, P. K.; Monroy, E.; Jegert, G.; Stutzmann, M.; Eickhoff, M. *Appl. Phys. Lett.* **2009**, *94*, 113108.

JA908848C