



Selective Detection of Hg(II) Ions from Cu(II) and Pb(II) Using AlGaN/GaN High Electron Mobility Transistors

H. T. Wang,^{a,*} B. S. Kang,^{a,*} T. F. Chancellor, Jr.,^a T. P. Lele,^a Y. Tseng,^a
F. Ren,^{a,**,z} S. J. Pearton,^{b,**} A. Dabiran,^c A. Osinsky,^c and P. P. Chow^c

^aDepartment of Chemical Engineering and ^bDepartment of Materials Science and Engineering,
University of Florida, Gainesville, Florida 32611, USA
^cSVT Associates, Eden Prairie, Minnesota 55344, USA

Bare Au-gated and thioglycolic acid functionalized Au-gated AlGaN/GaN high electron mobility transistors were used to detect mercury(II) and copper(II) ions. Fast detection of <5 s was achieved for thioglycolic acid functionalized sensors. The thioglycolic acid functionalization increased the sensitivity for detection of mercury by 2.5 times over the bare Au-gated surface. Both surfaces had a selectivity of approximately 100-fold over other contaminating ions of sodium, magnesium, and lead and can be easily recycled. Our results show that portable, selective, and fast Cu²⁺ and Hg²⁺ sensors can be realized by combining bare Au-gated and thioglycolic acid-functionalized surface in one sensor.

© 2007 The Electrochemical Society. [DOI: 10.1149/1.2778997] All rights reserved.

Manuscript submitted July 10, 2007; revised manuscript received August 6, 2007. Available electronically September 6, 2007.

The toxicity of heavy metal ions, including mercury(II) (Hg²⁺), lead(II) (Pb²⁺), copper(II) (Cu²⁺), and zinc(II) (Zn²⁺) has long been recognized as a chronic environmental problem.¹⁻⁵ In particular, mercury is released into the environment through a variety of courses, including the combustion of fossil fuels, mining, volcanic emissions, and solid waste incineration. Mercury and lead have attracted a great deal of attention around the world for its impact on wildlife ecology and human health. Certain bacteria convert inorganic Hg²⁺ ions into neurotoxic organic mercury compounds, which bioaccumulate through plants and the food chain, thereby affecting the entire ecosystem.^{6,7}

It is highly desirable to develop sensitive and selective analytical methods for the quantitative detection of heavy metal ions. These methods should be ideally portable so that they can be applied in different sites and environments. There are several traditional methods for heavy metal detection, including spectroscopic (AAS, AES, or ICP-MS) or electrochemical (ISE or polarography). However, these methods are either expensive or not useful for detection on site, where handheld portable devices could be very valuable.⁸⁻¹⁰ A number of selective heavy metal ion sensors have been devised utilizing redox, chromogenic, or fluorogenic changes. Most of these systems display shortcomings in practical use, such as interference from other metal ions and delayed response.¹¹⁻¹⁴ Therefore, the development of inexpensive methods for detection of bioavailable heavy metal concentrations is highly desirable.

GaN/AlGaN high electron mobility transistors (HEMTs) have been extremely useful for gas and liquid sensors for two key reasons. First, they consist of a high electron sheet carrier concentration channel induced by both piezoelectric polarization of the strained AlGaN layer and the difference in spontaneous polarization between AlGaN and GaN. Unlike conventional semiconductor field effect transistors, there is no intentional dopant in the AlGaN/GaN HEMT structure. The electrons in the two-dimensional electron gas (2DEG) channel are located at the interface between the AlGaN layer and GaN layer. Second, the electron carrier concentration strongly depends on the ambient.¹⁵⁻²² There are positive countercharges at the AlGaN/GaN HEMT surface layer induced by the 2DEG. Any slight changes in the ambient affects the surface charges of the AlGaN/GaN HEMT. These changes alter the 2DEG concentration in the AlGaN/GaN HEMTs. We have recently exploited these properties to detect a variety of species in gases and liquids using appro-

priately functionalized AlGaN/GaN HEMTs.¹⁵⁻¹⁹ For these reasons, nitride HEMTs are versatile devices that may be used for a variety of sensing applications.

In this paper, we report the detection of Hg²⁺ and Cu²⁺ ions with sensors fabricated with Au-gated and thioglycolic acid functionalized Au-gated GaN/AlGaN HEMTs. We investigated a wide range of concentration from 10 μM to 10 nM. The temporal resolution of the device was quantified along with limit of detection and selectivity over sodium, magnesium, and lead ions. The recyclability of the sensors between measurements was also explored.

The HEMT structures consisted of a 2 μm thick undoped GaN buffer and 250 Å thick undoped Al_{0.25}Ga_{0.75}N cap layer. The epi layers were grown by molecular beam epitaxy system on 2 in. sapphire substrates at SVT Associates. Mesa isolation was performed with an inductively coupled plasma (ICP) etching with Cl₂/Ar-based discharges at -90 V dc self-bias, ICP power of 300 W at 2 MHz and a process pressure of 5 mTorr. 50 × 50 μm ohmic contacts separated with gaps of 10, 20, and 50 μm consisted of E-beam-deposited Ti/Al/Pt/Au patterned by liftoff and annealed at 850°C, 45 s under flowing N₂ for source and drain metal contacts. 5 nm thin gold film was deposited as gate metal for two set of samples. One was for the bare Au-gate sensor and the other was for functionalizing a self-assembled monolayer of thioglycolic acid on the Au gate. An increase in the hydrophilicity of the treated surface by thioglycolic acid functionalization was confirmed by contact angle measurement, which showed a change in contact angle from 58.4 to 16.2° after the surface treatment, as shown in Fig. 1. 500 nm thick polymethyl methacrylate (PMMA) was used to encapsulate the source/drain regions, with only the gate region open to allow the liquid solutions to access the bare Au-gate or functionalized Au-gate surface. The source-drain current-voltage characteristics were measured at 25°C using an Agilent 4156C parameter analyzer with the Au-gated region exposed to different concentrations of Hg²⁺, Cu²⁺,

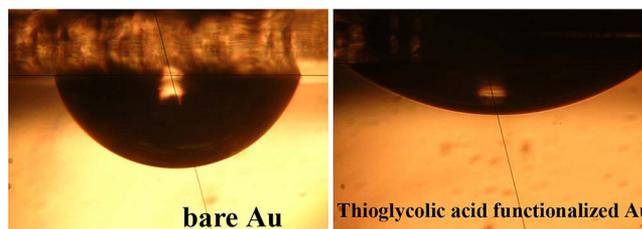


Figure 1. (Color online) Photographs of contact angle of water drop on the surface of bare Au (left) and thioglycolic acid functionalized Au (right).

* Electrochemical Society Student Member.

** Electrochemical Society Fellow.

^z E-mail: ren@che.ufl.edu

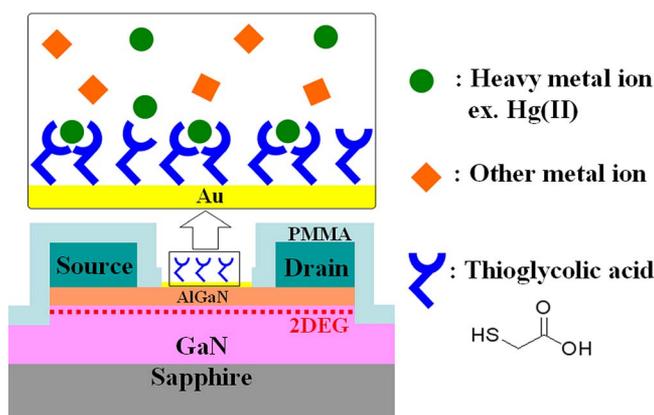


Figure 2. (Color online) A schematic of AlGaIn/GaN HEMT and the Au-coated gate area functionalized with self-assembled thioglycolic acids.

Pb^{2+} , Mg^{2+} , or Na^{+} solutions. AC measurements were performed to prevent side electrochemical reactions with modulated 500 mV bias at 11 Hz.

A schematic cross section of the device with Hg^{2+} ions bound to thioglycolic acid functionalized on the gold gate region is shown in Fig. 2. The thioglycolic acid, HSCH_2COOH , is an organic compound and contains functional groups of a thiol (mercaptan) and a carboxylic acid functional group. A self-assembled monolayer of thioglycolic acid molecule was adsorbed onto the Au gate due to strong interaction between gold and the thiol group for the functionalized sensors. The extra thioglycolic acid molecules were rinsed off with deionized (DI) water. XPS and electrical measurements confirmed a high surface coverage of thioglycolic acid molecules through Au-S bonding formation on the GaN surface, and the results have been previously published.¹⁹

Figure 3 shows the change in drain current of a bare Au-gated AlGaIn/GaN HEMT sensor and a thioglycolic acid functionalized AlGaIn/GaN HEMT sensor exposed to 10^{-5} M Hg^{2+} ion solutions as compared to exposed to DI water. The drain current reduction of the thioglycolic acid functionalized AlGaIn/GaN HEMT sensors was almost 80% more than that of the bare Au-gate sensor. The mechanism of the drain current reduction for bare Au-gate and thioglycolic acid functionalized AlGaIn/GaN HEMT sensors is probably quite different. For the thioglycolic acid functionalized AlGaIn/GaN HEMT, the thioglycolic acid molecules on the Au

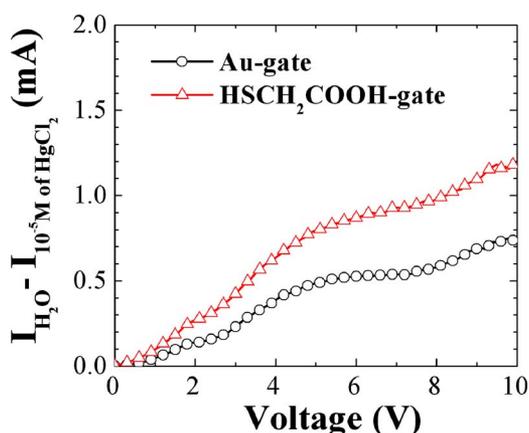


Figure 3. (Color online) Changes in HEMT drain-source current for bare Au-gate and Au-gate with thioglycolic acid functionalization exposed to 10^{-5} M Hg^{2+} ion solutions.

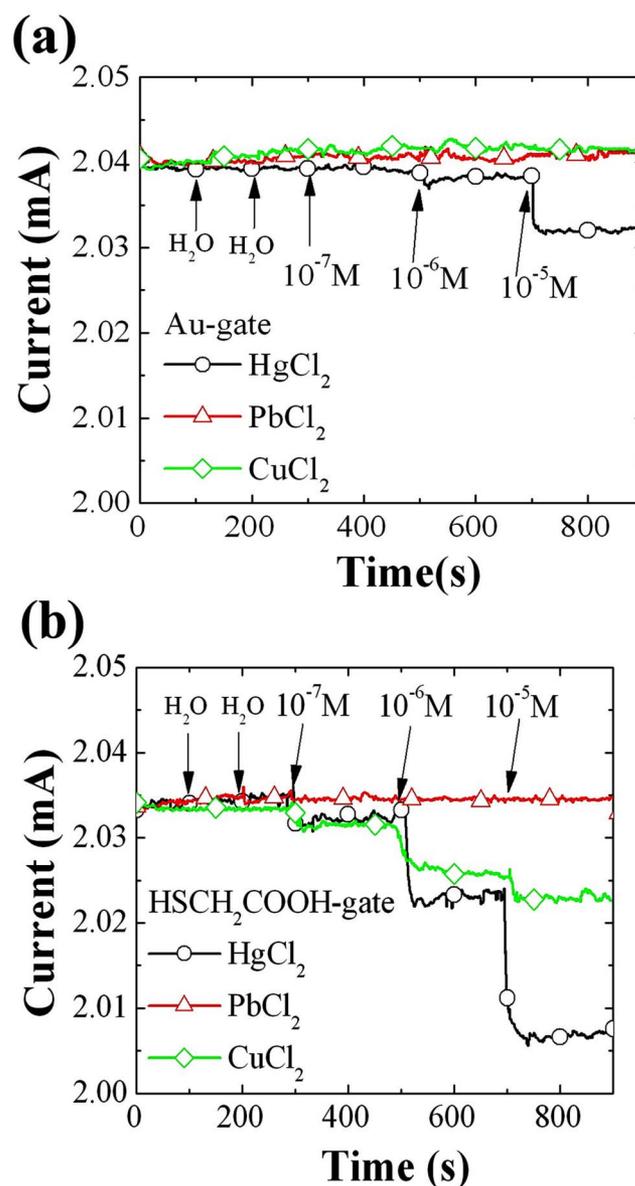


Figure 4. (Color online) (a) Time-dependent response of the drain current as a function of Hg^{2+} , Cu^{2+} , Pb^{2+} ion concentrations for bare Au-gate AlGaIn/GaN HEMT sensor. (b) Time-dependent response of the drain current as a function of Hg^{2+} , Cu^{2+} , Pb^{2+} ion concentrations for thioglycolic acid functionalized Au-gate AlGaIn/GaN HEMT sensor.

surface align vertically with carboxylic acid functional group toward the solution.²³ The carboxylic acid functional group of the adjacent thioglycolic acid molecules probably forms chelates $[\text{R-COO}^-(\text{Hg}^{2+})-\text{OOC-R}]$ with the Hg^{2+} ions. If the chelates are indeed forming, one would expect the charges of trapped Hg^{2+} ion in the $\text{R-COO}^-(\text{Hg}^{2+})-\text{OOC-R}$ to change the polarity of the thioglycolic acid molecules. This is probably why the drain current changes in response to mercury ions. A similar type of surface functionalization was used by Huang and Chang²⁴ and the detection performed with gold-nanoparticle-based fluorescence, but the detection time is longer than the nitride HEMT-based sensor. Because Hg^{2+} ions were used in our experiments, we do not expect an Au-mercury amalgam to form on the bare Au surface. The detailed mechanism for mercury ion-induced reduction in drain current of the Au-gate device is not clear and currently under further investigation.

Figure 4 shows time dependence of the drain current for the two

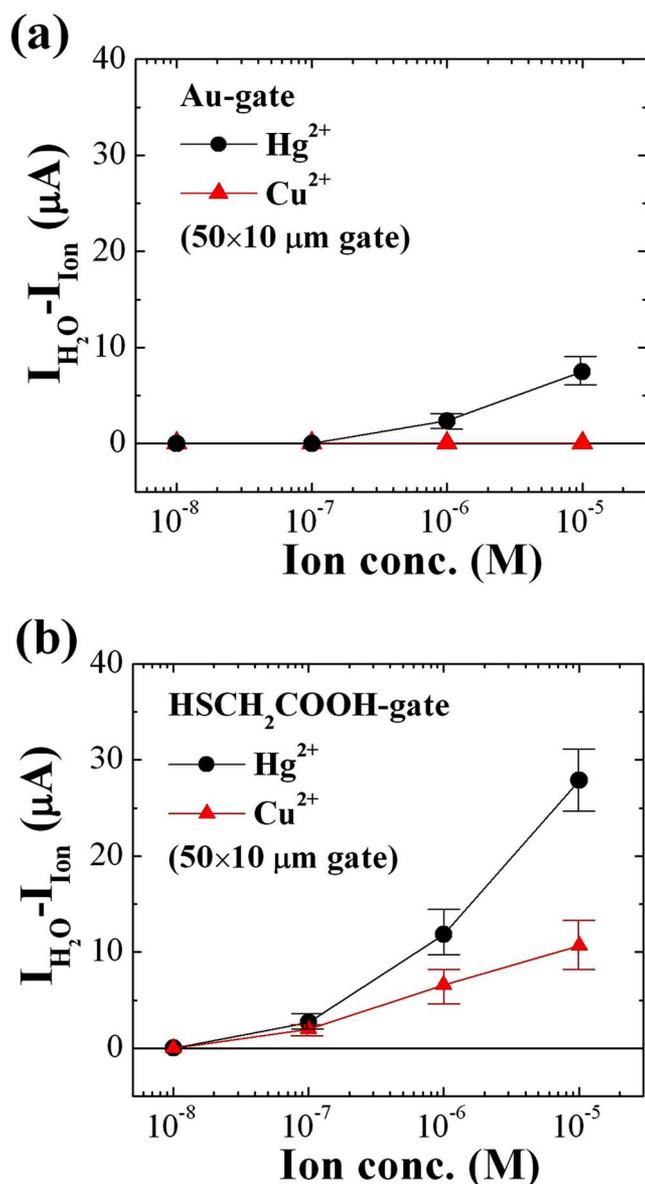


Figure 5. (Color online) Drain current changes in response to Hg^{2+} and Cu^{2+} ions as a function of the ion concentration for (a) the bare Au-gate and (b) the thioglycolic acid functionalized Au-gate AlGaIn/GaN HEMT sensor.

types of sensors for detecting Hg^{2+} , Cu^{2+} , and Pb^{2+} ions. Both types of sensors showed very short response time (<5 s), when exposed to Hg^{2+} ion solution. The limits of detection for Hg^{2+} ion detection for the bare Au-gate and thioglycolic acid functionalized sensors were 10^{-6} M and 10^{-7} M, respectively. Neither sensor could detect Pb^{2+} ions. For the Cu^{2+} ions, the detection limit of the thioglycolic acid functionalized sensor was $\sim 10^{-7}$ M. However, the bare Au gate could not detect the Cu^{2+} ions as shown in Fig. 4. Figure 5 shows the drain current changes in response to Hg^{2+} and Cu^{2+} ions as a function of the ion concentration for the two different surfaces. The difference in the response between the bare Au-gate and the thioglycolic acid functionalized sensors offers the possibility for selective detection for Hg^{2+} and Cu^{2+} ions presented in a single solution with a sensor chip containing both types of sensors, as shown in Fig. 6. The dimension of the active area of the AlGaIn/GaN HEMT sensor is less than $50 \times 50 \mu\text{m}$, and the sensors can be fabricated as an array of individual sensors. The fabrication of both sensors is identical except for the thioglycolic acid functionalized sensor,

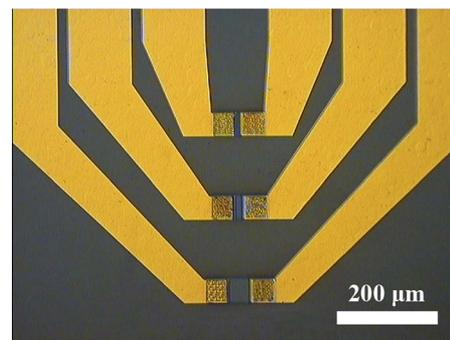


Figure 6. (Color online) Plain-view photograph of a multiple cell AlGaIn/GaN HEMT sensor.

which has an additional functionalization step. This step can be accomplished with microinkjet system to locally functionalize surfaces. The bare Au-gate and thioglycolic acid functionalized sensors also showed excellent sensing selectivity (over 100 times higher selectivity) over Na^+ and Mg^{2+} ions. As illustrated in Fig. 7, there was almost no detection of Na^+ and Mg^{2+} ions for both types of sensors with 0.1 M concentrations.

Most semiconductor-based chemical sensors are not reusable. The bare Au-gate and thioglycolic acid functionalized sensors showed very good reusability, as shown in Fig. 8. After a simple rinse with DI water, the sensors can be reused for Hg^{2+} ion detection repeatedly and the responses to different ionic solutions remain unchanged. The stability of thioglycolic acid functionalized Au surface is affected by several factors, such as oxygen level, light, initial packing quality, chain length, and terminal functional group.^{25,26} Our devices has been stored in nitrogen ambient and repeatedly used over a couple of weeks. The long-term stability of the thioglycolic acid functionalized Au surface is under investigation.

The current sensor operates at 0.5 V of drain voltage and 2 mA of drain current. However, the operation voltage and device size can be further reduced to minimize the power consumption to microwatt range. The sensor can be integrated with a commercially available handheld wireless transmitter to realize a portable, fast-response, and high-sensitivity Hg^{2+} and Cu^{2+} ion detector.

Conclusion

We have demonstrated bare Au-gate and thioglycolic acid functionalized AlGaIn/GaN HEMT sensors for heavy ion detection. The bare Au-gate sensor was sensitive to Hg^{2+} , and thioglycolic acid

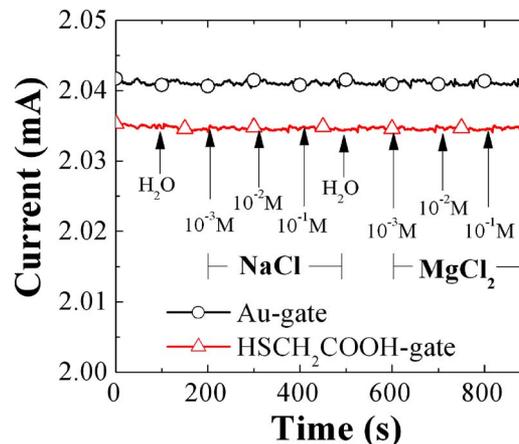


Figure 7. (Color online) Time-dependent change in the drain current in response to Na^+ and Mg^{2+} with a bare Au-gate and thioglycolic acid functionalized Au-gate HEMT sensor.

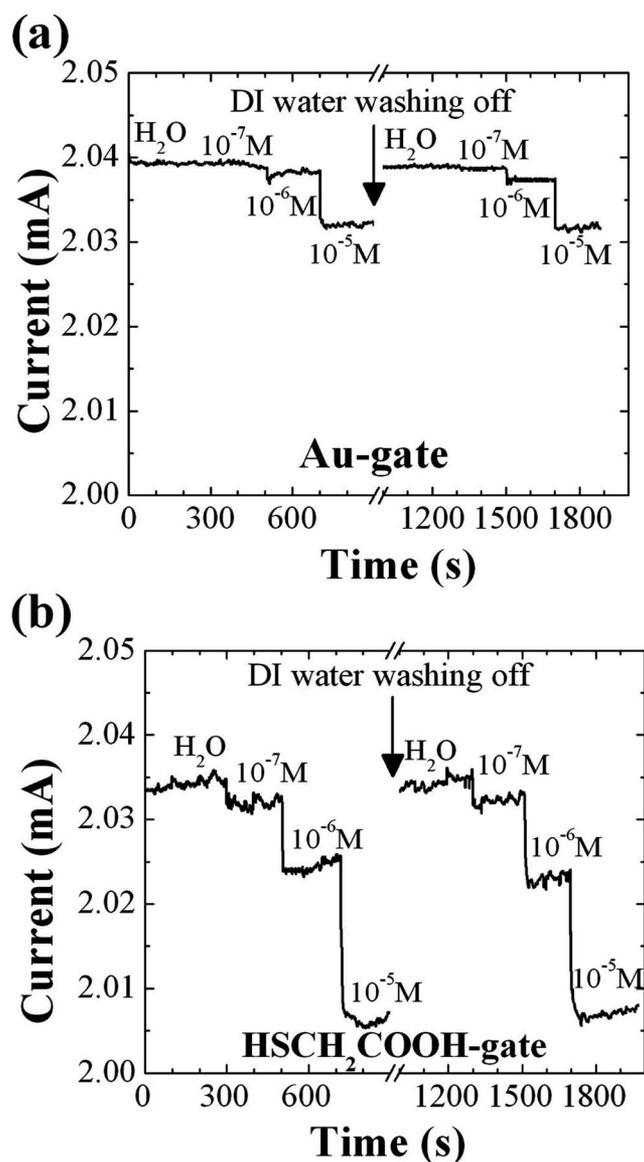


Figure 8. Recyclability for (a) the bare Au-gate and (b) the thioglycolic acid functionalized Au-gate surfaces.

functionalized sensors could detect both Hg²⁺ and Cu²⁺ ions. By fabricating an array of the sensors on a single chip and selectively functionalizing some sensors with thioglycolic acid, a multifunc-

tional specific detector can be fabricated. Such a sensor array can be used to quantitatively detect Hg²⁺ ions in Cu²⁺ ion solution or Cu²⁺ ions in Hg²⁺ ion solution. Both bare Au-gate and thioglycolic acid functionalized sensors can be repeatedly used after a simple DI water rinse.

Acknowledgments

The work at UF is partially supported by ONR grant no. N000140710982 monitored by Igor Vodyanoy, NASA Kennedy Space Center grant no. NAG 3-2930 monitored by Timothy Smith, and NSF grant no. DMR 0400416.

The University of Florida assisted in meeting the publication costs of this article.

References

1. A. Renzoni, F. Zino, and E. Franchi, *Environ. Res.*, **77**, 68 (1998).
2. J. M. Llobet, G. Falco, C. Casas, A. Teixido, and J. L. Domingo, *J. Agric. Food Chem.*, **51**, 838 (2003).
3. A. H. Stern, *Environ. Res.*, **98**, 133 (2005).
4. F. Zahir, S. J. Rizwi, S. K. Haq, and R. H. Khan, *Environ. Toxicol. Pharmacol.*, **20**, 351 (2005).
5. J. Mutter, J. Naumann, R. Schneider, H. Walach, and B. Haley, *Neuroendocrinol. Lett.*, **26**, 439 (2005).
6. W. Zheng, M. Aschner, and J.-F. Gherzi-Egea, *Toxicol. Appl. Pharmacol.*, **192**, 1 (2003).
7. I. Hoyle and R. D. Handy, *Aquat. Toxicol.*, **72**, 147 (2005).
8. A. L. Burlingame, R. K. Boyd, and S. J. Gaskell, *Anal. Chem.*, **68**, 599 (1996).
9. K. W. Jackson and G. Chen, *Anal. Chem.*, **68**, 231 (1996).
10. J. L. Anderson, E. F. Bowden, and P. G. Pickup, *Anal. Chem.*, **68**, 379 (1996).
11. A. Caballero, R. Martínez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tárraga, P. Molina, and J. Veciana, *J. Am. Chem. Soc.*, **127**, 15666 (2005).
12. E. Coronado, J. R. Galán-Mascarós, C. Martí-Gastaldo, E. Palomares, J. R. Durant, R. Vilar, M. Gratzel, and Md. K. Nazeeruddin, *J. Am. Chem. Soc.*, **127**, 12351 (2005).
13. Y. K. Yang, K. J. Yook, and J. Tae, *J. Am. Chem. Soc.*, **127**, 16760 (2005).
14. M. Matsushita, M. M. Meijler, P. Wirsching, R. A. Lerner, and K. D. Janda, *Org. Lett.*, **7**, 4943 (2005).
15. Hung-Ta Wang, B. S. Kang, F. Ren, R. C. Fitch, J. K. Gillespie, N. Moser, G. Jessen, T. Jenkins, R. Dettmer, D. Via, A. Crespo, B. P. Gila, C. R. Abernathy, and S. J. Pearton, *Appl. Phys. Lett.*, **87**, 172105-1-3 (2005).
16. B. S. Kang, S. Kim, F. Ren, J. W. Johnson, R. Therrien, P. Rajagopal, J. Roberts, E. Piner, K. J. Linthicum, S. N. G. Chu, K. Baik, B. P. Gila, C. R. Abernathy, and S. J. Pearton, *Appl. Phys. Lett.*, **85**, 2962 (2004).
17. B. S. Kang, F. Ren, L. Wang, C. Lofton, Weihong Tan, S. J. Pearton, A. Dabiran, A. Osinsky, and P. P. Chow, *Appl. Phys. Lett.*, **87**, 023508 (2005).
18. B. S. Kang, F. Ren, M. C. Kang, C. Lofton, Weihong Tan, S. J. Pearton, A. Dabiran, A. Osinsky, and P. P. Chow, *Appl. Phys. Lett.*, **86**, 173502 (2005).
19. B. S. Kang, J. J. Chen, F. Ren, S. J. Pearton, J. W. Johnson, P. Rajagopal, J. C. Roberts, E. L. Piner, and K. J. Linthicum, *Appl. Phys. Lett.*, **89**, 122102 (2006).
20. Y. Alifragis, A. Volosirakis, N. A. Chaniotakis, G. Konstantinidis, E. Iliopoulos, and A. Georgakilas, *Phys. Status Solidi A*, **204**, 2059 (2007).
21. O. Ambacher, M. Eickhoff, A. Link, M. Hermann, M. Stutzmann, F. Bernardini, V. Fiorentini, Y. Smorchkova, J. Speck, U. Mishra, W. Schaff, V. Tilak, and L. F. Eastman, *Phys. Status Solidi C*, **0**, 1878 (2003).
22. M. Eickhoff, J. Schalwig, G. Steinhoff, O. Weidemann, L. Görgens, R. Neuberger, M. Hermann, B. Baur, G. Müller, O. Ambacher, and M. Stutzmann, *Phys. Status Solidi C*, **0**, 1908 (2003).
23. F. Malem and D. Mandler, *Anal. Chem.*, **65**, 37 (1993).
24. C. C. Huang and H. T. Chang, *Anal. Chem.*, **78**, 8332 (2006).
25. M. H. Schoenfisch and J. E. Pemberton, *J. Am. Chem. Soc.*, **120**, 4502 (1998).
26. N. J. Brewer, T. T. Foster, G. J. Leggett, M. R. Alexander, and E. McAlpine, *J. Phys. Chem. B*, **108**, 4723 (2004).