

GaN Thin Film Based Light Addressable Potentiometric Sensor for pH Sensing Application

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Received January 9, 2013; accepted February 8, 2013; published online February 27, 2013

Gallium nitride (GaN) is a material with remarkable properties, including wide band gap, direct light emission and excellent chemical stability. In this study, a GaN-based light addressable potentiometric sensor (LAPS) with Si₃N₄ ~50 nm as a sensing membrane is fabricated. By modulated optical excitation from an ultraviolet 365 nm light-emitting diode, the photoresponse characteristic and related pH sensitivity of the fabricated GaN-based LAPS is investigated. A Nernstian-like pH response with pH sensitivity of 52.29 mV/pH and linearity of 99.13% is obtained. These results of the GaN-based LAPS show great promise and it could be used as a single chemical sensor or integrated optoelectronic chemical sensor array for biomedical research with high spatial resolution. © 2013 The Japan Society of Applied Physics

Semiconductor-based solid state detection devices are increasingly important for biosensor technology. Semiconductors provide a number of advantages such as high sensitivity, low power requirements, durability, multiplicity of measurement sites and the capability for miniaturization.¹⁾ Semiconductor-based sensors can be fabricated using mature fabrication technology of Si devices. Silicon-based sensors are still dominant due to their low cost, and reproducible and controllable electronic response. However, these sensors are not suitable for operation in extreme environments, for instance, in high temperature, high energy radiation condition, high pressure, or corrosive ambients. Wide band gap GaN-based material systems intensively studied over the last few decades²⁻⁴⁾ are alternative options to overcome the above mentioned limitations because of GaN's remarkable properties including excellent chemical stability and biocompatibility.⁵⁾ Silicon-based ion-sensitive field effect transistors (ISFETs) sensors, electrolyte-insulator-semiconductor (EIS) capacitive sensors⁶⁻⁹⁾ and III-V nitride-based ion sensitive sensors¹⁰⁻¹²⁾ have been widely studied. Among the variants of ISFET sensors, the measured ion concentration is an average over the entire sensing surface in contact with the whole solution. As an alternative sensing tool, a light addressable potentiometric sensor (LAPS) was first introduced by Hafeman et al. in 1988¹³⁾ by combining the scanned light pulse technique (SLPT)¹⁴⁾ with an EIS capacitor-based sensor. The unique feature of LAPS^{15,16)} is its addressing capability of an individual sensing site by utilizing a modulated light beam. The LAPS is also the basis of the chemical imaging¹⁷⁾ in which a focused laser beam scans the sensing area to visualize the two-dimensional distribution of the ion concentration. Most LAPS devices are Si based and are used for biosensing application. In this study, a thin-film GaN-based LAPS device is epitaxially grown and fabricated; its pH sensing performance is investigated by addressing with an ultraviolet 365 nm light-emitting diode operated at a frequency of 5 kHz.

An epitaxial GaN layer of 4 μm thickness with an n-type doping of $1.6 \times 10^{17} \text{ cm}^{-3}$ was grown by metal organic chemical vapor deposition on a 2-in. *c*-plane sapphire substrate. Samples of 1 cm × 1 cm size were cut from an epi-

wafer for sensor chip fabrication. After removing the native oxide from the GaN surface, a Ti/Al metal stack was deposited in a ring shaped outer region by electron beam evaporation using a shadow mask. This was followed by a subsequent rapid thermal annealing at 700 °C in N₂ ambient for ohmic contact formation. A 50-nm-thick layer of a Si₃N₄ sensing membrane was then deposited in the inside region of the Ti/Al ring by electron beam evaporation from 99.99% pure Si₃N₄ granules under 2×10^{-6} Torr chamber pressure. Finally, a poly(dimethylsiloxane) (PDMS) side wall was fabricated as a buffer solution container.

The pH value is of special importance in biological study, food technology, and medicine. For example, the pH value is used in the diagnosis of certain diseases and in determining the level of maturity in food. Figure 1(a) shows a schematic illustration of the layered structure of the fabricated LAPS device and the corresponding measurement setup. To measure the response of hydrogen ions (H⁺), commercially available pH buffer solutions from pH 2 to pH 12 are used. Prior to the measurement, the Si₃N₄ surface is activated by 1% HF solution for 10 s. A commercially available Ag/AgCl reference electrode is also used in the measurement. The generated photocurrent is detected by using a lock-in-amplifier (Stanford Research Systems SR510). The bias voltage sweep was provided through a data acquisition card (DAQ). The resulting photocurrent from the sensor chip is then recorded with a 16-bit DAQ card by a LABVIEW-based program on a PC. The original AC photocurrent signal is amplified and converted to photovoltage by a pre-amplifier with a conversion factor of $10^4 \text{ V} \cdot \text{A}^{-1}$. All the measurements are carried out in a black box to avoid room light interference. To test the performance of our GaN-based LAPS chips, an external 365 nm light-emitting diode modulated with a frequency of 5 kHz is used.

Also, as proposed and shown in Fig. 1(b), based on GaN the LAPS structure, further integration is possible by a double-side GaN thin film epitaxy followed by the back side LED fabrication or micro-LED¹⁸⁾ array fabrication. By grown this way, no external light source is needed and much more compact size LAPS devices can be obtained.

Figure 2(a) shows the original AC photocurrent signal and corresponding converted photovoltage as a function of

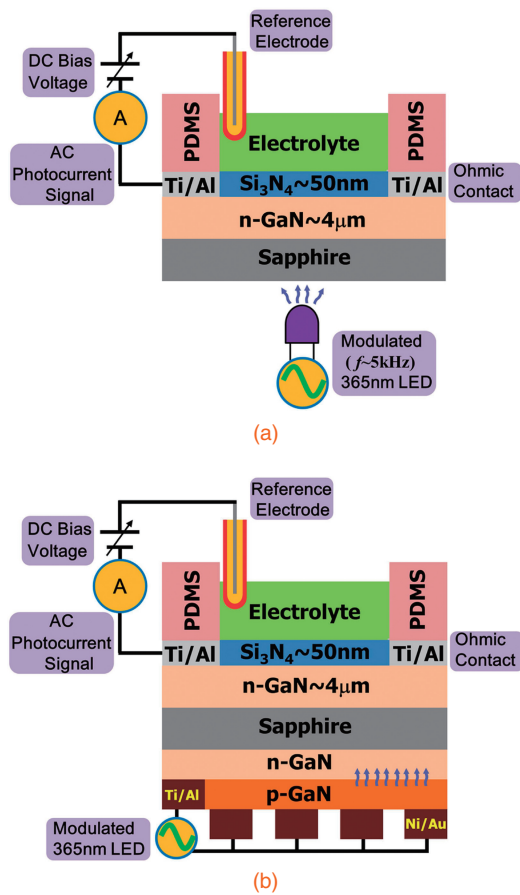


Fig. 1. (a) Schematic illustration of GaN-based LAPS structure and measurement setup. A positive value of bias potential indicates that the reference electrode (Ag/AgCl electrode) is biased positively with respect to GaN. An ultraviolet 365 nm light-emitting diode operated at 5 kHz frequency is used as a modulated optical excitation. (b) Proposed configuration to incorporate an LED array directly on the back side of the GaN-based LAPS device in the future.

reference bias potential in pH value of 7. Figure 2(b) shows the response of the GaN-based LAPS to different pH values from pH 2 to pH 12. The lower voltage of the reference bias corresponds to the depletion condition for n-GaN at the Si₃N₄ interface. Various biases correspond to different depletion conditions at the GaN–Si₃N₄ interface of our fabricated LAPS devices. The electron–hole pairs (EHPs) created by modulating optical excitation in n-GaN are separated in the electric field at the depletion region, and an alternating photocurrent is then generated and synchronized to the modulation frequency of the LED light source. In addition, the depletion width is also a function of surface potential or surface charge. Therefore, the depletion capacitance will vary with the surface potential. Of course, with a fixed resistance, photocurrent can be transformed into photovoltage. The normalized photovoltage–reference bias curve shifts along the voltage axis because of the change of surface potential at the interface of the sensing membrane (Si₃N₄) and solution with different concentrations of H⁺ present in pH buffer solution. As shown in Fig. 2(b), the normalized curves of the photovoltage versus reference bias shift along the bias axis are obtained clearly.

To calculate the pH sensitivity and linearity of the fabricated LAPS devices, the bias voltages corresponding to the

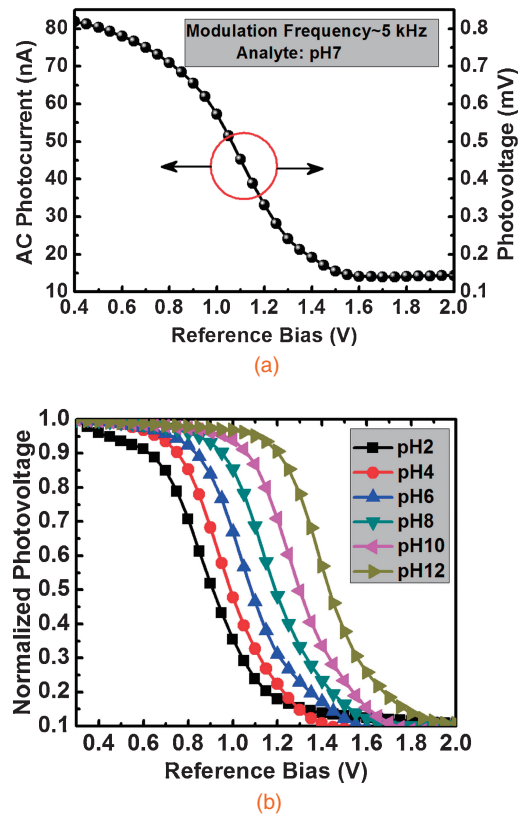


Fig. 2. (a) Measured AC photocurrent and corresponding converted photovoltage as a function of reference bias potential in pH 7. (b) Normalized photovoltage as a function of reference bias potential for different pH values is demonstrated. The lower voltage (to the left) corresponds to the depletion condition for the semiconductor at the insulator interface.

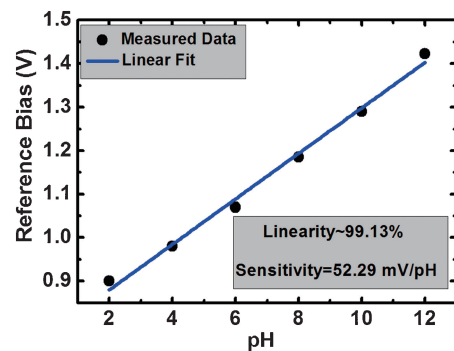


Fig. 3. Sensitivity and linearity characteristics of GaN/Si₃N₄ LAPS chip in the measured pH buffer solution are shown. A Nernstian-like pH response with pH sensitivity of 52.29 mV/pH and linearity of 99.13% is obtained.

inflection point of each curve in Fig. 2(b) are calculated and plotted in Fig. 3 as a function of the pH value. The resulting pH sensitivity and linearity are calculated and values as high as 52.29 mV/pH and 99.13% are obtained, respectively. These LAPS devices with an e-beam-deposited Si₃N₄ layer on top of the GaN semiconductor sensing structure show a nearly ideal Nernstian pH sensitivity, which is comparable to that of the traditional silicon-based LAPS device.¹⁹⁾

The LAPS pH detection is operated mainly by constant current detection mode,²⁰⁾ which monitors the change of inflection point voltage. Owing to some disadvantages of

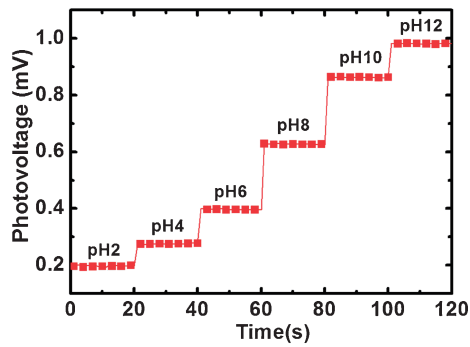


Fig. 4. Photovoltage is recorded with time at a constant reference bias voltage of 1.15 V during changes of pH value of the buffer solution (pH 2 → pH 12).

constant current mode measurement,²¹⁾ constant voltage mode LAPS is adopted in this work, which is more suitable for pH detection in practical application. Dynamic constant voltage mode measurement data are depicted in Fig. 4, which are obtained for characterizing our fabricated LAPS devices. In Fig. 4, the photovoltage is recorded as a function of time, at a constant reference bias voltage of 1.15 V and variation of buffer solution (pH 2 → pH 12). As shown in the Fig. 4, the fabricated GaN LAPS devices exhibit good response to the buffer solution variations.

An anion selective single-layer GaN potentiometric sensor was reported previously²²⁾ where Ga-polar GaN exhibited a Nernstian response to anions (SO_4^- and OH^-). In contrast, N-polar GaN exhibited a pH selective potentiometric response in a Nernstian manner for pH values from 2 to 10.²³⁾ This differences in the single-layer potentiometric structure behavior can be avoided in our GaN/ Si_3N_4 LAPS structure due to its surface being covered with a dielectric Si_3N_4 layer.

Furthermore, the spatial resolution of the LAPS is an important factor for the chemical imaging application. It has been demonstrated that the spatial resolution is determined by beam size and lateral diffusion of photogenerated EHP in the semiconductor substrate.^{24,25)} The lateral diffusion is determined by the thickness of the semiconductor layer and the diffusion length of the minority carrier. In the past, many attempts have been made to improve the spatial resolution of the LAPS device by thinning the Si substrate,²⁶⁾ using a silicon on insulator (SOI) substrate,²⁷⁾ using a GaAs substrate,²⁸⁾ and using an amorphous silicon thin film.²⁹⁾ In this study, the thickness of the GaN epitaxially grown film can be as small as 4 μm and the corresponding minority carrier diffusion length is around 280 nm.³⁰⁾ From the concept of spatial resolution in case of a thin semiconductor substrate,²⁵⁾ the spatial resolution of present GaN thin film LAPS is expected to be 4 μm or low depending on the epitaxial layer thickness and exploiting proper optical setup.

The initial pH results of these grown LAPS devices have usefully indicated the possibility of direct-band-gap GaN as the base semiconductor material for thin-film LAPS fabrication. Experiments to check their spatial resolution by means of a focused laser beam to replace the single external LED and some other aspect of sensors such as the drift phenomenon for practical usability are under progress.

In conclusion, a GaN-based LAPS device has been proposed, epitaxially grown, and fabricated. Its pH sensing properties have been demonstrated. A nearly ideal Nernstian pH sensitivity of 52.29 mV/pH is obtained from the fabricated GaN-based LAPS with a Si_3N_4 sensing membrane defined by the e-beam evaporation. Good linearity of 99.13% is observed. The fabrication processes are compatible with LEDs and can benefit their further integration. The thin-film-based structure can limit the diffusion of photogenerated EHPs in an epitaxially grown GaN layer and high spatial resolution for future biomedical image research can be expected.

Acknowledgment This work was supported by the National Science Council (NSC), Taiwan, under contract No. NSC-101-2221-E-182-047-MY2.

- 1) I. Karube: *Biosens. Fundamentals and Application* (Oxford University Press, Oxford, U.K., 1987) p. 471.
- 2) S. N. Mohammad and H. Morkoç: *Prog. Quantum Electron.* **20** (1996) 361.
- 3) S. J. Pearton, C. Zolper, R. J. Shul, and F. Ren: *J. Appl. Phys.* **86** (1999) 1.
- 4) R. M. Lin, M. J. Lai, L. B. Chang, and C. H. Huang: *Appl. Phys. Lett.* **97** (2010) 181108.
- 5) S. A. Jewett, M. S. Makowski, B. Andrews, M. J. Manfra, and A. Ivanisevic: *Acta Biomater.* **8** (2012) 728.
- 6) P. Bergveld: *IEEE Trans. Biomed. Eng.* **17** (1970) 70.
- 7) A. Poghosian, M. Thust, P. Schroth, A. Steffen, H. Lüth, and M. J. Schöning: *Sens. Mater.* **13** (2001) 207.
- 8) L. B. Chang, H. H. Ko, M. J. Jeng, Y. L. Lee, and C. S. Lai: *J. Electrochem. Soc.* **154** (2007) J150.
- 9) L. B. Chang, P. C. Chen, and M. J. Jeng: *J. Electrochem. Soc.* **157** (2010) G234.
- 10) B. S. Kang, H. T. Wang, F. Ren, B. P. Gila, C. R. Abernathy, S. J. Pearton, J. W. Johnson, P. Rajagopal, J. C. Roberts, E. L. Piner, and K. J. Linthicum: *Appl. Phys. Lett.* **91** (2007) 012110.
- 11) B. H. Chu, B. S. Kang, C. Y. Chang, F. Ren, A. Goh, A. Sciallo, W. Wu, J. Lin, B. P. Gila, S. J. Pearton, J. W. Johnson, E. L. Piner, and K. J. Linthicum: *ECS Trans.* **19** [3] (2009) 85.
- 12) M. S. Z. Abidin, A. M. Hashim, M. E. Sharifabad, S. F. A. Rahman, and T. Sadoh: *Sensors* **11** (2011) 3067.
- 13) D. G. Hafeman, J. P. Wallace, and H. M. McConnell: *Science* **240** (1988) 1182.
- 14) O. Engström and A. Carlsson: *J. Appl. Phys.* **54** (1983) 5245.
- 15) J. C. Owicki, L. J. Bousse, D. G. Hafeman, G. L. Kirk, J. D. Olson, H. G. Wada, and J. W. Parce: *Annu. Rev. Biophys. Biomol. Struct.* **23** (1994) 87.
- 16) C. H. Chin, T. F. Lu, J. C. Wang, J. H. Yang, C. E. Lue, C. M. Yang, S. S. Li, and C. S. Lai: *Jpn. J. Appl. Phys.* **50** (2011) 04DL06.
- 17) I. Lundström, R. Erlandsson, U. Frykman, E. Hedborg, A. Spetz, H. Sundgren, S. Welin, and F. Winquist: *Nature* **352** (1991) 47.
- 18) H. W. Choi, C. W. Jeon, M. D. Dawson, P. R. Edwards, and R. W. Martin: *MRS Proc.* **743** (2002) L6.28.
- 19) Y. H. Lin, A. Das, K. S. Ho, and C. S. Lai: *Proc. 6th IEEE Int. Conf. Nano/Micro Engineered and Molecular Systems*, 2011, p. 972.
- 20) T. Yoshinobu, H. Ecken, A. Poghosian, A. Simonis, H. Iwasaki, H. Lüth, and M. J. Schöning: *Electroanalysis* **13** (2001) 733.
- 21) N. Hu, C. Wu, D. Ha, T. Wang, Q. Liu, and P. Wang: *Biosens. Bioelectron.* **40** (2013) 167.
- 22) N. A. Chaniotakis, Y. Alifragis, A. Georgakilas, and G. Konstantinidis: *Appl. Phys. Lett.* **86** (2005) 164103.
- 23) K. H. T. Ba, M. A. Mastro, J. K. Hite, C. R. Eddy, and T. Ito: *Appl. Phys. Lett.* **95** (2009) 142501.
- 24) M. Sartore, M. Adami, C. Nicolini, L. Bousse, S. Mostarshed, and D. Hafeman: *Sens. Actuators A* **32** (1992) 431.
- 25) M. George, W. J. Parak, I. Gerhardt, W. Moritz, F. Kaesen, H. Geiger, I. Eisele, and H. E. Gaub: *Sens. Actuators* **86** (2000) 187.
- 26) M. Nakao, T. Yoshinobu, and H. Iwasaki: *Jpn. J. Appl. Phys.* **33** (1994) L394.
- 27) Y. Ito: *Sens. Actuators B* **52** (1998) 107.
- 28) W. Moritz, I. Gerhardt, D. Roden, M. Xu, and S. Krause: *Fresenius J. Anal. Chem.* **367** (2000) 329.
- 29) T. Yoshinobu, M. J. Schöning, F. Finger, W. Moritz, and H. Iwasaki: *Sensors* **4** (2004) 163.
- 30) Z. Z. Bandić, P. M. Bridger, E. C. Piquette, and T. C. McGill: *Appl. Phys. Lett.* **72** (1998) 3166.