Mater. Res. Soc. Symp. Proc. Vol. 1202 © 2010 Materials Research Society 1202-I06-02

A novel functionalization of AlGaN/GaN-ISFETs for DNA-sensors

S. Linkohr[1], S. U. Schwarz[2], S. Krischok[3], P. Lorenz[3], T. Nakamura[4], V.Polyakov[1], V. Cimalla[1], C. Nebel[1] and O. Ambacher[1]

[1] Fraunhofer Institute for Applied Solid State Physics, Tullastraße 72, 79108 Freiburg, Germany
[2] Albert-Ludwigs-University of Freiburg, Department of Microsystems Engineering (IMTEK) 79108 Freiburg, Germany
[3] Institute of Micro- and Nanotechnologies, Technical University Ilmenau, P.O. Box 100565, 98684 Ilmenau, Germany
[4] AIST Tsukuba Central 1 Tsukuba, Ibaraki 305-8561, Japan

Abstract

AlGaN/GaN pH sensitive devices were functionalized and passivated for the use as selective bio-sensors. For the passivation, a multilayer of SiO_2 and SiN_x is proposed, which stabilizes the pH-sensor, is biocompatible and has no negative impact on the following bio-functionalization. The functionalization of the GaN-surface was achieved by covalent bonding of 10-amino-dec-1-ene molecules by a photochemical process. After two different surface preparations islands of TFAAD are growing on the sensor surface by exposure with UV-light. In dependence on the surface pre-treatment and the illumination wavelength the first monolayer is completed after 3 h or 7 h exposure time dependent on the pre-treatment and illumination wavelength. Further exposure results in thicker films as a consequence of cross polymerization. The bonding to the sensor surface was analyzed by X-ray photoelectron spectroscopy, while the thickness of the functionalization was determined by atomic force microscopy scratching experiments. These functionalized devices based on the pH-sensitive AlGaN/GaN ISFET will establish a new family of adaptive, selective biomolecular sensors such as selective, reusable DNA sensors.

Introduction

Group III-nitrides are chemically stable semiconductors with high internal spontaneous and piezoelectric polarization. These characteristics allow the fabrication of very sensitive and robust bio-sensors to detect ions in gases and polar liquids, monitor bio-molecules and the bioactivity of cells in solution [1–5]. The strong polarization discontinuity at the AlGaN/GaN interface oriented along the [0001] axis results in a positive polarization charge. This interface charge is compensated by a two-dimensional electron gas (2DEG) located at the GaN side near the surface, which forms the conductive channel of a high-electron-mobility transistor (HEMT). A HEMT without gate metallization realizes an ion-sensitive field effect transistor (ISFET) by direct sensing of charged particles and molecules on the exposed gate area [9–11]. AlGaN/GaN-ISFETs have a high sensitivity and are the subject of intense investigation. They have emerged as attractive candidates for pH- and ion-sensitive sensors or detectors for biochemical processes [12–14]. These pH-sensors are the basis of the AlGaN/GaN-bio-sensors. By functionalization of the open gate, selectivity to specific biomolecules can be achieved such as for DNA molecules or proteins. To bio-functionalize GaN with DNA, the open gate was functionalized with 10-amino-dec-1-ene molecules by a photochemical method [15, 16]. Therefore two different treatments of the sensor surface were used. For the first tests the GaN was terminated with hydrogen by a hydrofluoric acid dip [17] and the second tests were arranged with an oxidized GaN-surface.

In this work, we investigate the functionalization process, the dependence on the illumination wavelength and the properties of the modified sensor surface. Special attention is given to the impact of the passivation, which has to protect the inactive sensor area and the contacts but should be biocompatible and chemically stable as well in the used electrolytes. The samples were analyzed with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and the sensor characteristics were monitored by titration experiments.

Experimental Details

The epitaxial growth of AlGaN/GaN heterostructures confining a 2DEG was accomplished by metal-organic chemical vapor deposition (MOCVD). On a thin GaN nucleation layer (25 nm) a 1.8 µm thick GaN layer is deposited to obtain the structural quality required for the 2DEG in the AlGaN/GaN heterostructure. The growth is completed with 22 nm $Al_{0.22}Ga_{0.78}N$ and a cap layer of 3 nm GaN, which enhances the chemical stability of the device. The location of the conductive channel only 25 nm below the surface permits an effective current modulation by manipulation of charges or electric fields at the sensor surface. For comparison of the functionalization process, GaN layers on SiC substrates were grown by MOCVD as well.

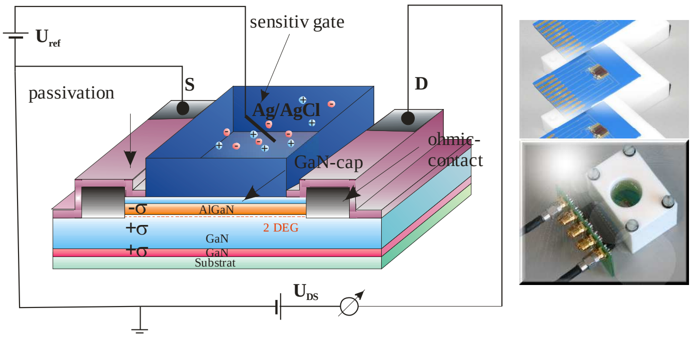
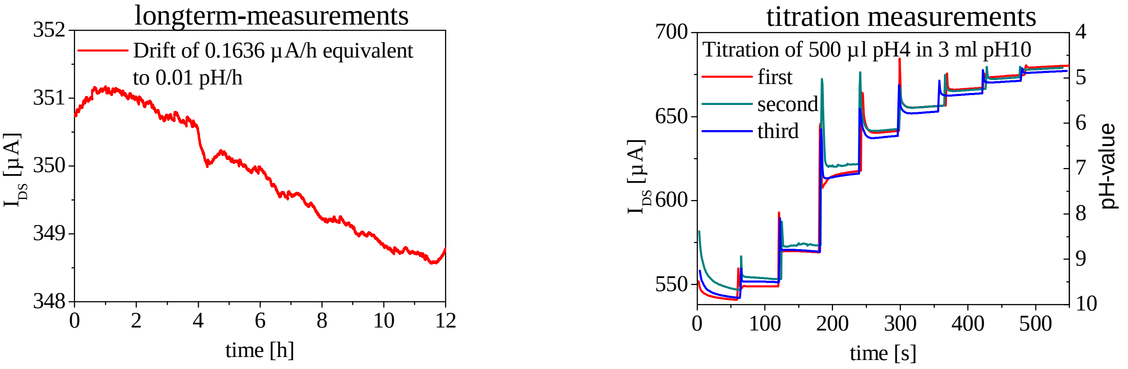


Figure 1: Schematic illustration of the sensor structure and measurement principle (left) and measurement setup (right).

pH-sensor The AlGaN/GaN-ISFETs result from leaving a bare GaN surface by omitting the gate metallization. To analyze the pH-sensor the gate was placed in an appropriate measuring solution. The definition of the potential of the solution is usually carried out by using a reference electrode (Fig. 1). This affects the surface charge by incident ions which enhance or deplete the 2DEG. At low pH, i.e. high concentration of H_3O^+, the surface acts as proton acceptor and causes the enhancement of the 2DEG. At high pH, i.e. high concentration of OH^-, it acts as proton donator and causes depletion of the 2DEG. With an achievable sensitivity (S) of 59 mV/pH these sensors are able to measure the pH-value at the Nernst limit. The sensors have to be appropriately protected with a passivation which has chemical stability in acidic and alkaline liquids. Various passivations such as SiO_2, SiN_x and a SiO_2-SiN_x-doublelayer with a thickness up to 500 nm were investigated. These layers reveal memory effects and ionic diffusion. A multilayer passivation composed of SiO_2(150 nm)-SiN_x(150 nm)-SiO_2(150 nm)-SiN_x(150 nm) shows the best chemical stability in long-term-(Fig. 2a.) and titration-measurements (Fig. 2b.). Table 1 shows the comparison of the various passivations.



a) b)

Figure 2: The AlGaN/GaN-ISFET with a multilayer passivation shows the best chemical stability in long-term- and titration-measurements. a) long-term-measurements revealing a drift of 0.02 pH/h. b) repetition accuracy of the titration-measurements.

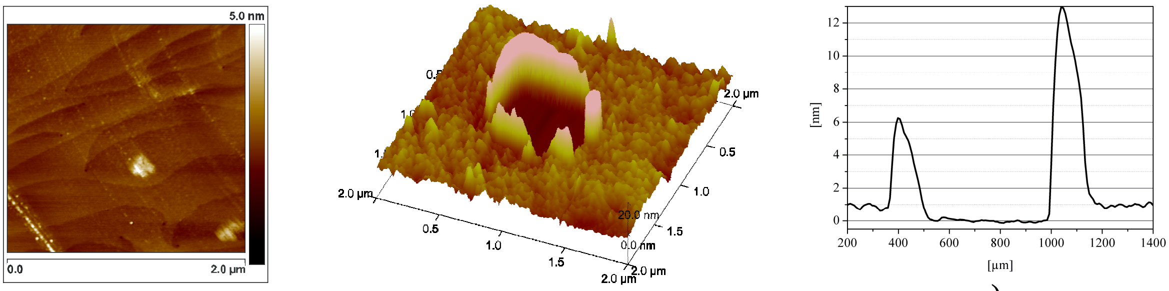
Table 1: The comparison of the different investigated passivations clarifies the best chemical stability of the multilayer passivation.

Passivation	Thickness [nm]	Drift [µA/h]	Drift [pH/h]
SiN_x	500	25.9	1
SiO_2-SiN_x-doublelayer	500	18	1
SiO_2-SiN_x-SiO_2-SiN_x-layer	700	12.6	0.9
SiO_2-SiN_x-SiO_2-SiN_x-layer	600	0.2	0.01

Bio-sensors To bio-functionalize GaN with DNA, the open gate region with an active area of 0.04 – 3 mm^2 was pretreated. For the hydrogen terminated surface the sample was dipped for 5 min in 2% hydrofluoric acid. This method has three benefits: it terminates the surface with hydrogen, the sample is purged from organic contamination and the functionalization is faster. For the oxidized surface the samples were oxidized in air. The 10-amino-dec-1-ene molecules, which are used for functionalization, are passivated at one side with a trifluoroacetic acid group $(CH_2{=}CH(CH_2)_8\text{-}NHCOCF_3)$ (TFAAD). To obtain covalent bonding of the olefin molecules, a photochemical method is used. The GaN-surface was illuminated with a UV lamp for different times in a nitrogen filled chamber after wetting with TFAAD. The illumination was realized in two different ways. On the one hand the samples were irradiated with the whole spectrum of the UV-lamp. On the other hand the spectrum was filtered. The filter limited the wavelength and let pass 200 to 400 nm of the UV-spectrum. After illumination, the samples were cleaned in chloroform, isopropanol and DI-water for 3 min in an ultrasonic bath. Then the samples were analyzed with AFM and XPS.

Results and discussion

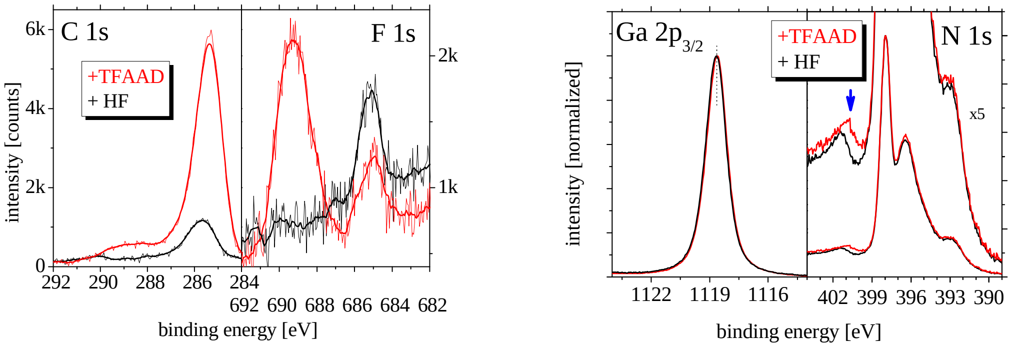
By using UV-radiation hydrogen atoms were removed from the surface. The result is an electrostatic interaction with the electron rich double bonds of TFAAD, which results in the formation of a C-Ga-bond. The resulting carbocation is an unstable intermediate, and is saturated by hydrogen from a bordering Ga-atom [18]. By the binding of only one TFAAD-molecule-layer with a length of about 15 Å [19] a monolayer of about 1.5 nm thickness is formed. After different exposure times the samples were analyzed with AFM and XPS. The measurements showed that the first amines are already linked at the GaN-surface after only 30 min UV-radiation which is seen in the AFM-picture in figure 3a. By extending the exposure time, more TFAAD molecules are bonded forming islands with increasing diameter until the first monolayer is completed. These monolayers were further analyzed by AFM-scratching-experiments (figure 3b and c) and XPS. The scratching experiments were made in contact-mode. The functionalized film was removed with a force of 100 to 200 nN. Figure 3b shows a scratched GaN-surface, the area, where scratching removed the monolayer appears dark while the detached TFAAD-molecules form a bright border. These experiments allow the measurements of the thickness of the TFAAD-layer.



a) b) c)

Figure 3: AFM images of the GaN-surface a) the first amines are already linked after 30 min. After scratching: b) 3D morphology, c) line scan across the centre revealing the thickness of the TFAAD-layer on the GaN-surface.

The bonding of the TFAAD-molecules is illustrated in the XPS results in figure 4a by comparing the fluor- and the carbon-peak before (black) and after (red) the functionalization. The HF cleaned sample exhibits typical structures for GaN with some minor F and C adsorbates as illustrated in figure 4a. The XPS results indicate a successful functionalization with TFAAD-molecules. For compensation of charging effects the spectra were shifted to a reference binding energy of the Ga $2p_{3/2}$ state to 1118.6 eV. Most evident is the appearance of a new F 1s component at 689 eV binding energy, which is caused by the CF_3 group of the TFAAD [15]. In parallel the expected changes in the C1s emission, namely a strong rise at about 285.5 eV caused by the alkyl chain is observed. The carbon atoms of the TFAAD in a different chemical environment cause the additional intensity at higher binding energies.

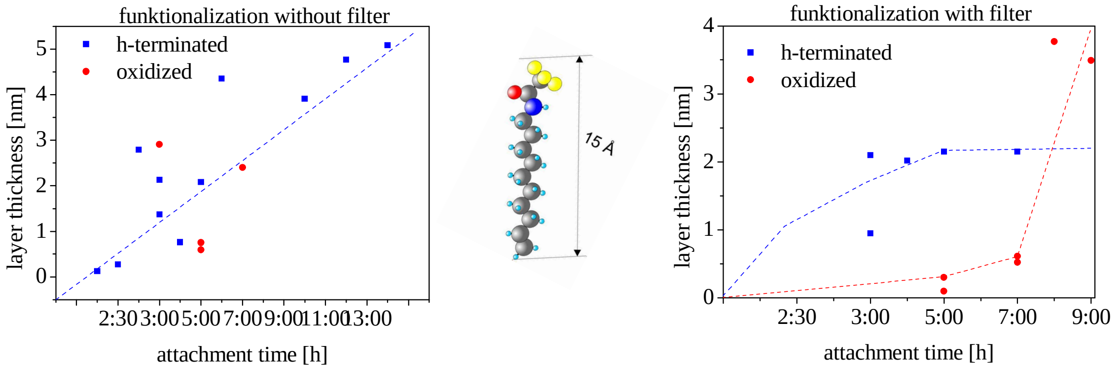


a) b)

Figure 4: The XPS (mon. Al Kα) measurements of bio-functionalized GaN surfaces (a) comparison of the adsorbate-induced F 1s and C 1s core levels emission (b) Ga $2p_{2/3}$ and N 1s spectra. The spectra were shifted to a reference binding energy of the Ga $2p_{3/2}$ state of 1118.6 eV for compensation of charging effects.

Moreover, the functionalization procedure leads only to minor changes in GaN substrate related states, the core levels of the N 1s and the Ga $2p_{3/2}$ are shown in figure 4b. The Ga $2p_{3/2}$ core level exhibits no significant changes, while the N 1s spectrum a small new component at 400.5 eV is observed. This state is most likely related to the NH component of the TFAAD-molecule. Note, that the indicated binding energies are with respect to the Fermi level of the sample holder and might be affected by a slight surface charging.

Due to the fact that the illumination was realized in different ways we have to compare the different effects on the functionalization. On the one hand the samples were irradiated with the whole spectrum of the UV-lamp. The result is shown in figure 5a, it is clearly visible that the TFAAD-molecules are linked faster then with filtered illumination. Because of the fast pre-cross-polymerization caused by the visible light there are no reproducible measurements. An influence of the HF- or oxygen-treatment cannot be detected. On the other hand the spectrum was filtered. The filter let pass the UV-spectrum between 200 and 400 nm (figure 5b). There is an influence of the pre-treatment of the surface shown in figure 5b. The monolayer on the H-terminated surface is achieved faster (blue line) than on the oxidized surface (red line). The measurements of a 2 nm layer thickness by achieving the first monolayer results because of the roughness of the surface. By prolongation of the exposure, more TFAAD-layers are linked to the GaN-surface in consequence of polymerization.



a) b)

Figure 5: The comparison of the dependency of the different photochemical exposure and the different pre-treatments of the GaN-surface: the illumination a) without filter b) with filter.

Conclusion

The presented results demonstrate that the H-terminated and the oxidized GaN-surface can be functionalized by olefin-molecules by using a photochemical exposure. It was demonstrated that the resulting thickness of the TFAAD-layer is dependent on the time and the wavelength of the exposure. The resulting surface is the starting point for the functionalization of the pH-sensors. Such GaN/AlGaN/GaN-devices are promising bio-sensors because of the particularly good bonding stability of bio-molecules to GaN. This could be used for very robust and chemical stabile bio-sensors and DNA-sensors.

Acknowledgements

The authors would like to acknowledge the assistance of Nadine Geldmacher, Gudrun Kaufel, Mechthild Korobka, Brigitte Wieber, Arnulf Leuther and Brian Raynor. This work was supported by the Fraunhofer Attract program and the Fraunhofer "Doktorandinnenprogramm: Mehr Frauen in die angewandte Forschung". The authors also would like to thank the help of the ZMN in Ilmenau which is supported by the BMBF Optimi.

References

1. O. Ambacher, J. Phys. D: Appl. Phys. 31, 2653–2710 (1998).
2. S.J. Pearton, J.C. Zolper, R.J. Shul, F. Ren, J. Appl. Phys. 86, 1–78 (1999).
3. S.C. Jain, M. Willander, J. Narayan, R. Van Overstraeten, J. Appl. Phys. 87, 965–1006 (2000).
4. M. Stutzmann, G. Steinhoff, M. Eickhoff, O. Ambacher, C.E. Nebel, J. Schalwig, R. Neuberger, G. Müller, Diamond Relat. Mater. 11, 886–891 (2002).
5. M. Eickhoff, J. Schalwig, G. Steinhoff, O. Weidemann, L. Görgens, R. Neuberger, M. Hermann, B. Baur, G.Müller, O. Ambacher, M. Stutzmann, Phys. Stat. Sol. (c), 1908–1918 (2003).
6. O. Ambacher, J. Smart, J.R. Shealy, N.G. Weimann, K. Chu, M. Murphy, W.J. Schaff, L.F. Eastman, R. Dimitrov, L. Wittmer, M. Stutzmann, W. Rieger, J. Hilsenbeck, J. Appl. Phys. 85, 3222–3233 (1999).
7. J.P. Ibbetson, P.T. Fini, K.D. Ness, S.P. DenBaars, J.S. Speck, U.K. Mishra, Appl. Phys. Lett. 77, 250–252 (2000).
8. O. Ambacher, M. Eickhoff, A. Link, M. Hermann, M. Stutzmann, F. Bernardini, V. Fiorentini,Y. Smorchkova, J. Speck, U. Mishra,W. Schaff,V. Tilak, L.F. Eastman, Phys. Stat. Sol. (c), 1878–1907 (2003).
9. R. Neuberger, G. Müller, O. Ambacher, M. Stutzmann, Phys. Stat. Sol. (a) 185, 85–89 (2001).
10. G. Steinhoff, M. Hermann, W.J. Schaff, L.F. Eastman, M. Stutzmann, M. Eickhoff, Appl. Phys. Lett. 83, 177–179 (2003).
11. M. Bayer, C. Uhl, P.Vogl, J. Appl. Phys. 97 (2005).
12. B.S. Kang, F. Ren, L. Wang, C. Lofton, W. Tan Weihong, S.J. Pearton, A.Dabiran, A. Osinsky, P.P. Chow, Appl.Phys. Lett. 87 (2005).
13. G. Steinhoff, B. Baur, G. Wrobel, S. Ingebrandt, A. Offenhäusser, Appl.Phys. Lett. 86 (2005).
14. Y. Alifragis, A. Georgakilas, G. Konstantinidis, E. Iliopoulos, A. Kostopoulos, N.A. Chaniotakis, Appl. Phys. Lett. 87, (2005).
15. H. Kim, P.E. Colavita, K.M. Metz, B.M. Nichols, B. Sun, J. Uhlrich, X. Wang, T.F. Kuech, R.J. Hamers, LANGMUIR 22 (19), 8121-8126 (2006)
16. T. Strother, R.J. Hamers, L.M. Smith, Nucleic Acids Research, 28, 3535–3541 (2000).
17. S.W. King, J.P. Barnak, M.D. Bremser, K.M. Tracy, C. Ronning, R.F. Davis, R.J. Nemanich., J. Appl. Phys., 84, 5248–5260 (1998).
18. C.L. Hu, J.Q. Li, Y. Chen, W.F. Wang, Journal of Physical Chemistry C, 112(43), 16932–16937 (2008).
19. N. Yang, H. Uetsuka, H. Watanabe, T. Nakamura, C.E. Nebel Chemistry of Materials 19 (2007) 2852-2859