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# Gallium Nitride-Based Potentiometric Anion Sensor

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**The gallium nitride (GaN) semiconductor is used as the sensing element for the development of a potentiometric anion sensor. The anion recognition mechanism is based on the selective interaction of anions in solution with the epitaxial Ga-face polarity GaN (0001) wurtzite crystal film grown on sapphire. The native GaN crystal is used for the development of an ion blocked sensor. The potential is based on the Volta potential, generated at the semiconductor/solution interface and within the Helmholtz layer, due to specifically adsorbed anions. The selectivity of the sensor is based on the direct interaction of the anionic ligand with the outer electron-defective gallium atoms; thus, it is not dependent on the lipophilicity of the adsorbed charged species. The chemical resistivity of the GaN crystal provides sensors with excellent lifetime, signal stability, and reproducibility.**

The optimization of ion-selective electrodes (ISEs) is a major task in recent years. One of the major problems is to determine the optimum experimental conditions under which all thermodynamic and kinetic parameters influence the analytical characteristics of the ISE, such as the detection limit and operational stability. To this, the extensive models described so far have played a considerable role.<sup>1</sup> On the other hand, the location and the origin of the potential-generating processes is still an unresolved issue 30 years later. One of the major problems contributing to this matter is the limited work performed with well-controlled interfaces. Almost all ISEs employ sensor elements that are based, at least partly, on ion exchange reactions, which provide the permselectivity of the membrane, as well as the potential development mechanism. Due to the fact that such membranes have a potential generated mechanism that is based on both the Volta potential (blocked interfaces) on the outer membrane interface and the Galvani potential (unblocked interfaces) on the inner membrane interface, a clear understanding of the sensor behavior is very difficult to deconvolute.

It is well known that the vast majority of potentiometric ISEs are based on liquid polymeric membranes that are doped with

organic or organometallic ionophores.<sup>2–9</sup> Existing ionophore-based anion selective sensors usually suffer from low selectivity, short lifetime, and most of all poor stability. At the same time, the response mechanism of these systems is usually not very clear, since it consists of outer membrane potential (Volta potential), surface potential, and inner membrane potential (Galvani potential).<sup>10,11</sup>

Solid-state sensor elements are valuable tools for both the development of chemical sensors and potential generating studies due to their well-defined semiconductor surface/solution interfaces. One of the few examples of such material in existence is that of the lanthanum fluoride crystal, which is used for the development of the well-known fluoride-selective sensor.<sup>12</sup> This material can also be used as gate in ISFETs, for the development of fluoride-selective CHEMFETs.<sup>13,14</sup> A very interesting study using a single crystal was presented almost 15 years ago by Umezawa et al.<sup>15</sup> In that paper, Cd-face cadmium sulfide single crystals were used for the development of a face-specific anion-sensitive potentiometric sensor. A short analysis of the potential generating process of this crystal raised numerous questions, most of which are still unanswered today. The main issue is the mode of potential generation on the surface of such crystal, knowing that there is no ion permeation within the inner layer. Surface analysis studies indicated that there is indeed a selective anion interaction of the

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S<sup>2-</sup> ion with the cadmium metal. It was also shown that the surface quality of the sensor, as well as the binding affinity of the surface with the anion, determines the observed sensor sensitivity.

The so-called III-nitride material systems have been the subject of intense research lately. Their unique physical and chemical properties allow for their application in a variety of industrial environments. Gallium nitride-based high-electron-mobility transistor devices have been developed for a variety of microelectronic and high-temperature gas sensor applications.<sup>16,17</sup> In such heterostructures, a two-dimensional electron gas manifold forms a sheet of ionic charge at the free GaN surface. The surface of the (0001) GaN wurtzite crystal is characterized by the fact that each gallium atom has three bonds to the underlying nitrogen atomic plane, while it is available for ligation on the outer face. Recent studies<sup>18</sup> have proven that these gallium atoms are relatively electron defective, due to the induced polarity of the Ga to the N bond. It has been shown that this property induces considerable Lewis acidity to the outer gallium atoms, making them reactive toward many Lewis bases,<sup>19</sup> starting from water to thiols and organic alcohols. The similarity of the GaN semiconductor to that of CdS provides the grounds for using this surface for the design of a new potentiometric anion sensor.

## EXPERIMENTAL SECTION

**GaN Sensor Fabrication.** The Ga-face GaN (0001) films were grown on Al<sub>2</sub>O<sub>3</sub> (0001) either by molecular beam epitaxy (MBE) using a radio frequency (RF) nitrogen plasma source (RFMBE) or by a combination of RFMBE and metalorganic vapor-phase epitaxy (MOVPE).<sup>17,20</sup> In the latter case, a 0.5- $\mu$ m film was grown on commercially available MOVPE GaN/Al<sub>2</sub>O<sub>3</sub> (0001) templates, using optimized growth conditions for step-flow growth. All the GaN samples were undoped. The optimized tuning of the RFMBE growth allowed for the development of a smooth GaN surface characteristic of a step-flow growth mechanism, as shown by atomic force microscopy. The wafer was then scribed to pieces approximately 5 by 5 mm. A 0.1-mm-diameter platinum wire was bonded with indium at the edge of the GaN. The bonding pad, the sides, and the backside were covered with epoxy glue, leaving only the GaN surface exposed to the solution. There is no pretreatment of the sensors prior to testing.

**Electrochemical Measurements.** All reagents were purchased from commercial suppliers and were of analytical grade. In all experiments, Nanopure water (~18 M $\Omega$  easy pure model D7033, Barnstead) was used. Potentiometric measurements were performed with a Lawson Labs Inc. EMF16 Precision Electrochemistry interface, versus a double-junction reference electrode (90-02, Thermo Orion). The signal was recorded via a personal computer using the L-EMF DAQ 2.5 software. The pH response experiments were performed in 0.1 M tris(hydroxymethyl)-aminomethane solution, to which aliquots of 0.1 M HCl were

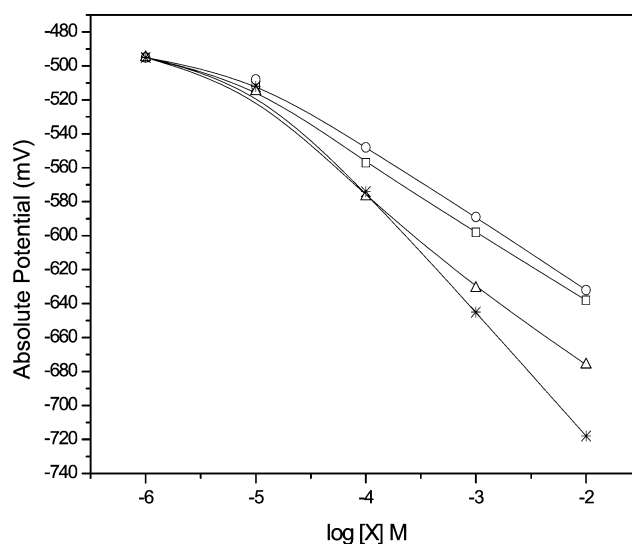


Figure 1. Calibration curves of the GaN-based sensor to four different potassium salts: (○) KF, (□) KCl, (△) KNO<sub>3</sub>, and (\*) KSCN.

added in order to decrease the pH. The pH of the solution was monitored using a calibrated pH glass electrode (81-72 BN, Thermo Orion). The calibration curves for the different salts were obtained using the standard additions method, while activity coefficients were calculated using the Debye–Huckel equation. For all potentiometric measurements, aliquots from the 0.1 M stock solution of each salt were added to 50 mL of deionized water, and the potential was monitored with a frequency of 1 Hz. The impedance spectra were obtained using an Autolab PGSTAT 30 potentiostat/galvanostat equipped with a frequency response analyzer (Eco Chemie). A sinusoidal excitation signal with potential amplitude of 10 mV RMS and a frequency range of 0.1 Hz–100 kHz at a base potential of 0.0 mV was applied versus a Ag/AgCl double-junction reference electrode (model 90-02, Orion), while 1-cm<sup>2</sup> platinum (model 96-78-00, Orion) was used as the counter electrode.

## RESULTS AND DISCUSSION

The selectivity to anions of the GaN-based potentiometric sensor was performed in water, to which aliquots of salt solutions were added. Due to the fact that the resistance of the GaN sensor element is low, there are no significant problems arising from measurements in low ionic strength environments. The calibration curves of the sensor to some anions are shown in Figure 1. The overall potentiometric response to all anions tested is presented in Table 1. As can be seen from the data presented in Figure 1 and Table 1, the observed sensitivity and selectivity (based on either overall response or slope) is different for each anion tested. The lipophilicity of the anions does not seem to play a major role in the selectivity of the sensor.

The observed potentiometric response of the GaN-based sensor to anions can be justified by the fact that the Ga-face GaN (0001) surface has three complete bonds to nitrogen atoms of the underlying atomic plane and one remaining bond “unbound”,<sup>21</sup>

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(21) Unbound atoms are characterized the terminal gallium atoms in the GaN crystal structure. Based on the crystal structure, the coordination sphere of the gallium is incomplete and can thus coordinate to existing electro-negative species.

Table 1. Total Potentiometric Response and Selectivity Coefficients ( $\log K_{\text{Cl},\text{X}}^{\text{pot}}$ ) of the GaN-Based Sensor to a Range of Potassium or Sodium Salts Tested for a Concentration Change between 0 and 0.1 M in Water

salt	total potentiometric response (0–0.1 M)	selectivity coefficients $\log K_{\text{Cl},\text{X}}^{\text{pot}}$
KSCN	–227	1.94
sodium salicylate	–224	1.87
KI	–223	1.84
KClO <sub>4</sub>	–192	1.12
KNO <sub>3</sub>	–186	0.98
KBr	–179	0.81
CH <sub>3</sub> COOK	–159	0.35
KCl	–144	
KF	–140	0.09

which is expected to make the gallium atoms Lewis acidic, as has been shown previously.<sup>18</sup> In this work,<sup>18</sup> it has been calculated that the atomic charge of the outer gallium is 0.691 while that of the nitrogen is –1.382. The dipole moment also is toward the gallium ( $\mu = 1.314$ ), and the traceless atomic quadrupolar moment tensor ( $\mathbf{Q}_b$ ), along the internuclear axis, is 1.825 and 5.046 for the gallium and nitrogen atoms, respectively. The gallium atoms are electron defective due to nitrogen atoms and thus susceptible to coordination with species, such as anions.

To investigate the mechanism of the above potentiometric response, it is essential to elucidate the way of the potential generation. It is known that the potentiometric measurement of a well-defined interface is related to the flat band potential ( $V_{\text{fb}}$ ) of that interface. Such measurements can provide information on the potential distribution at semiconductor/electrolyte interfaces and can be related to the amount of the charged species adsorbed at that interface.<sup>22</sup> It has also been known that  $V_{\text{fb}}$  shifts positively or negatively depending on the sign of excess surface charge, which is caused by specific adsorption of ionic species<sup>23</sup> at the outer surface. The magnitude of this potential is a function of the sum of the initial flat band potential and the difference in potential upon the development of the Helmholtz layer in different electrolytes. This potential is represented as  $V_{\text{fb}} = V_{\text{fb},0} + \Delta V_{\text{H}}$ , where  $V_{\text{fb},0}$  is the value of  $V_{\text{fb}}$ , without specific adsorption, and does not depend on the concentration of the nonactive ligands in the solution. On the other hand, the second term  $\Delta V_{\text{H}}$  does depend on the amount of selectively adsorbed ions within the inner Helmholtz layer, as has been shown for the case of CdS.<sup>15</sup> If the  $V_{\text{fb},0}$  remains constant, the changes in the measured potential of a single-crystal interface are equal to the  $\Delta V_{\text{H}}$ . In other words, if the surface of a crystal can selectively interact with charged species, the observed potentiometric response is due to the preferential adsorption of the specific ions in the Helmholtz layer. Under these conditions, the response time of the sensor should be fast and reversible. This has also been suggested by Buck,

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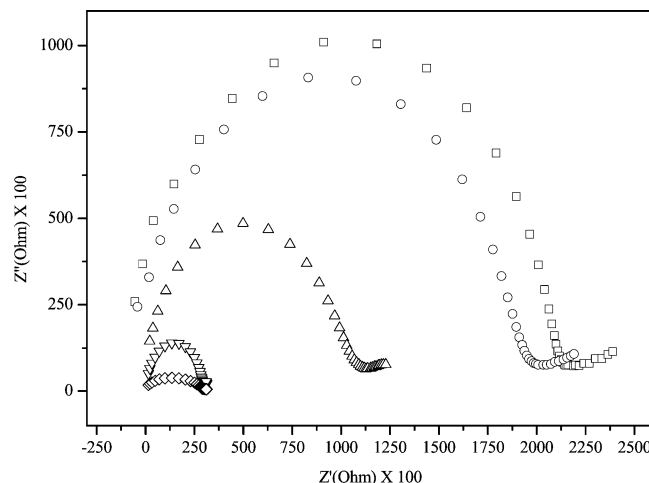


Figure 2. Impedance spectra of GaN-based sensor in different KCl solutions: ( $\square$ )  $10^{-6}$  M KCl, ( $\circ$ )  $10^{-5}$  M KCl, ( $\Delta$ )  $10^{-4}$  M KCl, ( $\nabla$ )  $10^{-3}$  M KCl, and ( $\diamond$ )  $10^{-2}$  M KCl. 10 mV RMS at zero base potential in a frequency range between 0.1 Hz and 100 kHz.

since the model is similar to the so-called fixed site ion exchange mechanism.<sup>1</sup>

In the case that the potential generated is based on the selective adsorption of charged species within the Helmholtz layer, the slope of a sensor will depend on the  $\Delta V_{\text{H}}$  value. It has been shown that this value is proportional to the surface excess charge due to the specific adsorption of ions and reversely proportional to the double layer capacitance. Under low-activity conditions and if a simple adsorption equilibrium exists, one gets the Nernst equation, and a slope of 59.2 mV/decade for monovalent ions. On the other hand, if there is a limiting number of adsorption sites and interaction between the adsorbates, the slope is not the one expected from the Nernst equation. The Helmholtz layer capacity  $C_{\text{H}}$ , the number of adsorption sites, the surface coverage of the adsorbants, and the energy of interaction between adsorbants are some of the parameters that affect the slope of the potentiometric response. Surface imperfections will have a drastic effect on the slope of the sensor, since under such conditions the co-ion exclusion mechanism fails.

Figure 2 shows the impedance spectra of the GaN-based sensor as a function of different activities of KCl in solution. The effect of the activity increase on the increase of the layer capacitance as expected from theory is very pronounced. In addition, the spectra are very stable over time, while their reversibility indicates that a fixed site ion exchange mechanism at the surface is taking place, as suggested by Buck.<sup>1</sup>

To prove that the potential generation is based purely on the Helmholtz layer, the logarithm of the square of the capacitance of the outer interface as a function of the logarithm of KCl activities is plotted in Figure 3. In this figure, the measured potential is also plotted on the same graph. The excellent relationship between these two values proves that the observed potential is only due to the ionic layer developed at the outer interface and within the Helmholtz layer. This also proves the fact that the observed anion sensitivity is based on the interaction of the anions with the surface of the GaN crystal.

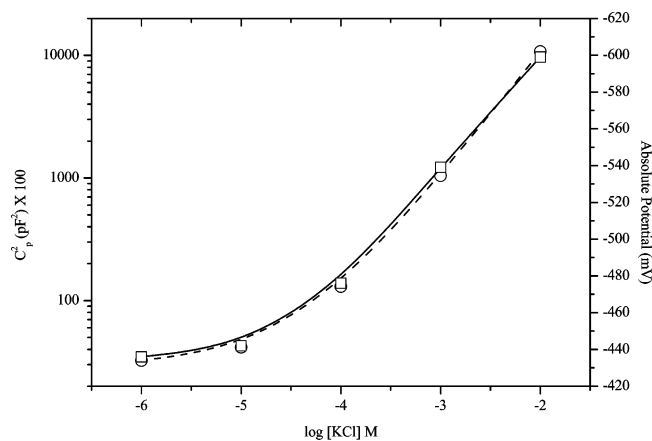


Figure 3. XYY graph of the square of the interfacial capacitance  $C_p$  ( $\square$ ) as a function of KCl activity on the left Y axis and measured potential ( $\circ$ ) on the right Y axis of the GaN sensor.

It has been suggested that the sensitivity of a semiconductor surface can be expressed using the following expression:<sup>24</sup>

$$\frac{d\Delta V_H}{d \ln[\alpha]} = \frac{ZF\Gamma}{\left[ \frac{1}{\{\theta(1-\theta)\}} + f + \frac{Z^2 F^2 \Gamma}{C_H RT} \right]} C_H$$

This is based on the Frumkin isotherm for adsorption, where  $Z$  is the charge,  $F$  is the Faraday constant,  $\Gamma$  is the number of adsorption sites,  $\theta$  is the surface coverage of adsorbates, and  $f$  is the energy of interaction between the adsorbed species. Based on this equation, the sensitivity, and thus the selectivity if calculated using the separate solution method, is related to the quality of the surface and the surface coverage, and inversely proportional to the capacity, and the interaction between the anions. The difference in the  $C_H$  values of these materials explains this difference in the sensitivity. It was also determined that the sensitivity of the sensor to anions decreased considerably when the crystal was not cleaned carefully after each use. Such data indicate the importance of the active sites present on the outer surface, since impurities can drastically decrease this value, a fact that is detrimental to the observed sensitivity.

A characteristic and unique property of the GaN crystal is its extremely high stability. The crystal structure cannot under any wet chemical conditions be etched or destroyed.<sup>25</sup> Etching of the GaN surface can be performed to a limited degree only under photoelectrochemical activation<sup>26</sup> and in very corrosive environments. Based on this fact, it is expected that the potential of the GaN sensor will be very stable over time. Indeed, the signal stability of the sensor over time is excellent, since there was no significant potential drift when the sensor was immersed in electrolyte solution for up to 5 days as shown in Figure 4.

The response time of a solid-state sensor is also of importance, since such information is not only analytically useful but it can also provide information on the mode of the measured potential

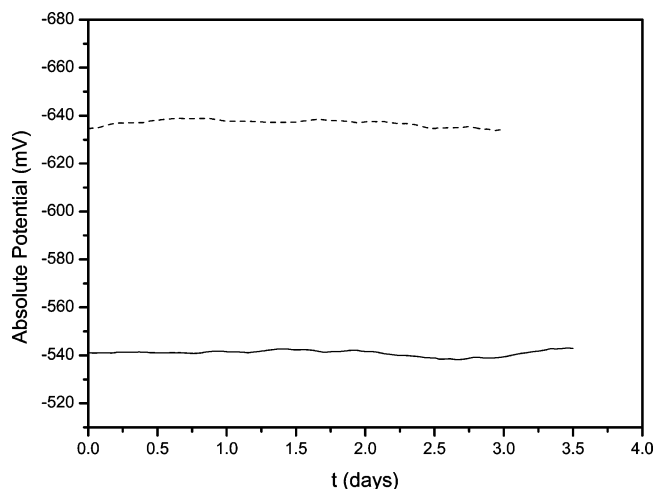


Figure 4. Signal stability of the sensor in  $10^{-2}$  (dash) and  $10^{-4}$  M (solid) KCl solution.

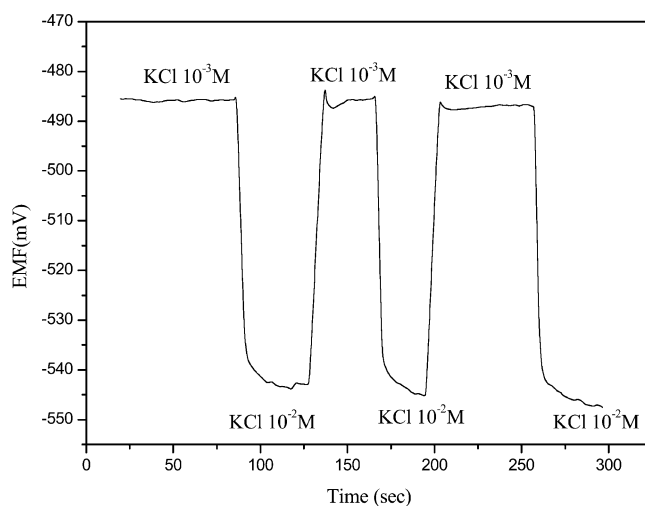


Figure 5. Chart recording of the GaN-based sensor response to two different KCl concentrations.

buildup. It is expected that since there is no bulk transport within the GaN crystal, the surface will have a well-defined interface with the solution. Thus, the response time and baseline return of such sensors should be very fast. From the response time studies in Figure 5 it is observed that the response time and baseline return of the sensor to activity changes in potassium salt solutions are very fast and within the time required for the mixing of the solution. The fast response time of the GaN crystal, together with the stable potential over a prolonged period of time, further proves the fact that the observed potentiometric response is a purely surface phenomenon. It is mandatory though that the surface remains clean down to atomic level, to achieve the optimum sensitivity and detection limit to anions.

## CONCLUSIONS

Gallium nitride crystal grown on sapphire substrate is shown to be an electroactive material with unique properties as a sensing element for the development of anion-sensitive potentiometric sensors. In this paper, we demonstrate that the gallium atoms of the outer surface of the GaN (0001) crystal coordinate selectively and reversibly with anions in solution. It is shown that the anion

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coordination generates interfacial potential, which is related to the activity of the anions. It is shown that the interfacial capacity is related to the anion activity in solution and to the observed potentiometric response of the sensor. However, direct correlation of the observed selectivity of the sensor to the electronegativity of the anionic ligands used, their Lewis basicity, and their lipophilicities, as well as to the exact coordination of the exposed gallium layer, necessitates further extensive investigations. The GaN-based sensor has excellent stability and reversibility, providing the grounds for both its application as the platform for fundamental surface potentiometric studies and as generic sensor

element for the development of sensors for ion chromatography and  $\mu$ -TAS applications.

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