

GaN / AlGa_N Semiconductors for DNA Biosensors – An Overview

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Abstract: *Electrochemical devices have attracted attention due to their low cost and simplicity, but significant improvements in their sensitivities are still needed for use with clinical samples. Wide band-gap group III nitride compound semiconductors (Al/GaInN materials system) are alternative options to supplement silicon in these applications because of their chemical inertness, high temperature/high power capability, high electron saturation velocity and simple integration with existing GaN based UV light emitting diode, UV detectors and wireless communication chips. The conducting 2DEG channel of AlGa_N/GaN HEMTs is very close to the surface and extremely sensitive to adsorption of analytes. HEMTs sensors can therefore be used for detecting gases, ions, pH values, proteins, and DNA. This paper gives an overview on the use of GaN /AlGa_N heterostructures for DNA biosensor applications.*

Keywords: GaN, AlGa_N, Heterostructures, DNA Biosensors, HFET

1. Introduction

Over the last three decades group III nitrides semiconductor materials have been studied extensively for their applications in Light Emitting Diodes [LED's], high temperature/power devices and chemical, gas and biological sensors [1-3.] Some of the common group III nitride semiconductors are Gallium nitride [Ga_N], Indium nitride [In_N], Boron nitride [BN] and Aluminum gallium nitride [AlGa_N]. The first Gallium Nitride [Ga_N] based light emitting diode was reported in the seventies [4.] The pioneering research on nitride semiconductors by Pankove, Akasaki, Nakamura and many others established the potential applications of these semiconductors in optoelectronics. The primary reasons that enable nitride semiconductors to be used in high temperature, voltage and high power devices are a large band gap discontinuity of 3.39eV, a high peak electron velocity, saturation velocity [3×10^7 cm/sec] and a high thermal and chemical stability [5]. Gallium Nitride has been researched extensively for the past three decades for its application in Light Emitting Diodes [LED's], power devices and UV photodetectors.

The group III-N semiconductors can exist in three crystal structures Wurtzite, Zinc blende and rock salt structure. In ambient conditions the thermodynamically stable structure for bulk Ga_N, AlN and InN is the wurtzite crystal structure. Ga_N, AlN and InN can be grown in the rock salt structure under very high pressure. In the wurtzite structure Ga_N, AlN and InN have a band gap of 3.4, 6.2 and 1.9 eV respectively at room temperature [6.] A wurtzite crystal structure consists of 2 interpenetrating hexagonal close packed structures each with one type of atom offset along the c axis by 5/8 of the cell height [7].

It was only in the 1990's that high quality defects free Ga_N was successfully grown using Metal Organic Chemical Vapor Deposition [MOCVD]. These procedures used either Ga_N or AlN as nucleation materials [8-9.] As the growth methods improved and the unintentional doping was reduced, it was possible to do intentional doping. Silicon and Germanium were used for n-type doping of Ga_N. Initially there were a few setbacks in the p-type doping of Ga_N. These problems were overcome by

Amano et al [10] who used Magnesium to dope Ga_N p type by Low Energy Electron Beam Irradiation [LEEBI]. Ga_N and AlN are chemically and thermally very stable. Even though their thermal stability is exploited in high temperature devices their chemical stability poses certain difficulties since the well established wet processes cannot be applied to them.

One has to use only dry etching during their processing. Chlorine [Cl₂] based discharge is commonly used to etch Ga_N. Ga_N and its alloy AlGa_N form heterostructures that offer a high mobility [>1300 cm²/v-sec] and a high density electron gas [1×10^{13} /cm²] without any intentional doping. This property is useful in application ranging from chemical and biological sensors to fast switching devices. [11]

With the recent developments in crystal growth technology and the ability to control the doping there has been an increased interest in hetero structures formed between Gallium nitride and its alloy Aluminum Gallium Nitride. Due to the combined effect of spontaneous and piezoelectric effects these hetero structures can form a high density and a high mobility electron gas channel without any intentional doping. This high density electron gas makes these hetero structures ideal to be used as sensors. Another unique property is the excellent chemical stability of Ga_N. Ga_N which has no known wet etchants. This is the reason why FET's [Field effect transistors] of Ga_N and its alloy AlGa_N are also used as biosensors. [12-14].

Added to these advantages the lack of inversion symmetry leads to a very strong polarization effect in nitride materials [table 1]. Using this property and combining the effects of piezoelectric polarization present due to the strain induced by the lattice and thermal mismatch between AlGa_N and Ga_N, it is possible to achieve a two dimensional electron gas density [2DEG] as high as 10^{13} cm⁻² at the interface without resorting to any intentional doping. In order to achieve this, normally a thin layer of AlGa_N is grown on a relatively thick layer of Ga_N. For such a wurtzite AlGa_N/Ga_N heterostructure the piezoelectric polarization of the thin AlGa_N layer is five times as high as the AlGaAs/GaAs heterostructures. This

contributes to a significant increase in the sheet carrier concentration at the interface [15- 16]. Apart from this the spontaneous polarization effect of the group III nitrides in the wurtzite crystal structure is very high. The combination of these two types of polarization leads to a macroscopic electric field responsible for the creation of the interface sheet charge.

Table 1

Spontaneous Polarization	AlN	GaN	InN
P0 [Cm ⁻²]	-0.081	-0.029	-0.032

2. Spontaneous and Piezoelectric Polarization

Nitrides lack inversion symmetry and exhibit piezoelectric polarization when strained along the [0001] direction [17]. The piezoelectric coefficient of nitrides is almost an order of magnitude higher than the other III-V materials [18]. In GaN a basal surface can be Ga face or N face. It can therefore be either the [0001] face or the [0001] face conventionally representing the Ga face or the N face respectively. These two faces differ in their physical and chemical properties [19].

In the absence of any external electric fields the polarization value [P] of AlGa_xN or GaN is given by

$$P = P_{SP} + P_{PE} \text{-----} [1] [5]$$

Where

PSP= Spontaneous polarization= $P_{SP}z$

PPE= Strain Induced polarization= $e_{33}z + e_{31}(x + y)$

The relation between x , y and z is

$$z = -2C_{13}/C_{33}(x + y) \text{-----} [2]$$

Here

C_{13} and C_{33} are elastic constants and e_{33} and e_{31} are piezoelectric coefficients.

Using these equations the piezoelectric polarization is given as,

$$P_{PE} = 2(x + y)[e_{31} - e_{33}C_{13}/C_{33}] \text{-----} [3]$$

$[e_{31} - e_{33}C_{13}/C_{33}] < 0$ for AlGa_xN and therefore $P_{PE} < 0$ for tensile and > 0 for compressive strain respectively. The spontaneous polarization of AlN and GaN are both negative [20].

Because of the differences in the structural parameters between GaN and AlN, spontaneous polarization is higher in AlN as compared to GaN. The values of the piezoelectric coefficients and the electric constants are given in Table 2.

Table 2: Piezoelectric coefficients of AlN, GaN and InN

Material	AlN	GaN	InN
e_{33} [Cm-2]	1.46	0.73	0.97
e_{31} [Cm-2]	-0.60	-0.49	-0.57
$[e_{31}-e_{33} [C_{13}/C_{33}]]$	-0.86	-0.68	-0.9

As shown in Figure 1 piezoelectric and spontaneous polarizations are pointing in the same direction in the case of tensile strain and in the opposite direction in the case of compressive strain. This variation in polarization leads to the creation of a charge density. A 2DEG or a 2DHG will be formed at the interface to compensate for these polarizations induced charges, depending on whether the polarization induced charge is positive or negative. The sheet charge density is a function of the Al content x in Al_xGa_{1-x}N and increase as x increases. For example as x increases from 0.15 to 0.3 the calculated sheet charge density increases from 0.013 to 0.027C/m².

The minimum sheet resistivity for an intentionally undoped AlGa_xN/GaN with $x=0.3$ is around 190Ω. Such low values of sheet resistivity combined with thermal stability, high saturation velocity and high sheet carrier concentration make these heterostructures ideal for high power and high frequency applications [20].

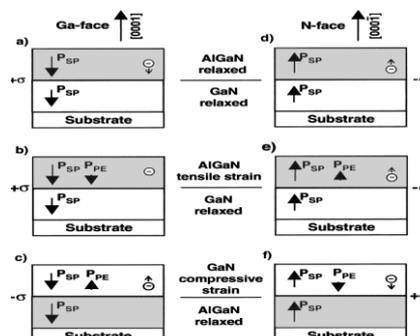


Figure 1: Direction of spontaneous and piezoelectric effect in AlGa_xN/GaN heterostructures

At lower frequencies AlGa_xN/GaN HEMTs are being pursued for power switching applications, biological and chemical sensors. A biosensor is an analytical device whose biological sensing element detects the presence of a target analyte and produces an electrical signal in proportion to the analytes concentration [21].

A biosensor can be designed to be sensitive to changes in surface charge density, mass, change in pH, light emission etc. The sensor device can signal this change in the form of a change in current, potential, mass etc. These sensors can be integrated with electronic devices and this field is broadly called as “bioelectronics” [22].

3. DNA and DNA Sensors

Watson and Crick described the structure of the DNA in 1953 [23]. The DNA is made of repeating units of 4 basic nucleotide bases, adenine, guanine, cytosine and thymine. The DNA is coiled up to form a double stranded helical structure with 2 ss-DNA’s held together by hydrogen

bonds. The structure of the DNA can be maintained as single stranded by either applying heat or if it is maintained at a high pH. When these conditions are not maintained 2 ss-DNA's with complementary bases will reanneal to form a dsDNA with adenine pairing with cytosine by 2 hydrogen bonds and guanine with thymine with 3 hydrogen bonds.

In biosensors the probe is an ssDNA sequence, which represents a particular biological species. These sequences are normally between 20-40 bases long. The probe is chosen so that it binds to specific regions from the target probe. Short probes are chosen because they take less time to hybridize but unfortunately they are more prone to nonspecific binding. Another difficulty being faced is difficulty in attaching labels to short probes. These DNA bases as compared to enzymes or antibodies are stable and easy to synthesize in the laboratory [24-26]. Nucleic acid based probes can also be used to identify genetic mutations or changes in the cellular materials [27].

4. FET based Deoxyribonucleic Acid [DNA] Sensor

The need for a nucleic acids analysis in a fast and reliable manner is generated because of their need in genetics, diagnoses of diseases [28] and in food safety. The commonly used methods like radio labelling and fluorescence based detection are time consuming and difficult to implement because of the complexities involved in carrying out these reactions and are also difficult to quantify and to transmit the data. A FET based DNA sensor is label free and overcomes some of the above-mentioned problems. The basic mechanism for a FET based sensor is the DNA hybridization event. In DNA hybridization a probe ssDNA binds with the target DNA, which is also single stranded by forming a dsDNA helix structure with the help of hydrogen bonds. The unique complementary nature of binding between the base pairs namely adenine-thymine and cytosine-guanine is the basis for the DNA hybridization process [29].

In the event of the immobilization of the ssDNA or its hybridization with the complementary ssDNA the charge associated with the DNA alters the electric potential acting on the gate region of the FET. This change in electric potential is reflected as a change in the drain current or the threshold voltage of the FET. DNA is negatively charged in aqueous solutions because of their phosphate background, this charge would affect the charge density in the space charge region of the semiconductor. The change in the current and the detection time has varied depending on the DNA immobilization density [30], immobilization procedure and the buffer solutions used [31-33].

Initially silicon was used as the material for fabricating semiconductor biosensor. Silicon based FET's had certain drawbacks like lack of chemical stability, need of a reference electrode to apply the bias voltage and the problem of not being able to maintain the activity of the biomolecules on the silicon surface. AlGaIn/GaN heterostructures due to their chemical and thermal stability proved to be an excellent substitute for silicon. The chemical stability of GaN ensures that there would be

minimum degradation of bio-molecules adsorbed on it. We can also easily integrate this sensor with a GaN based light emitting diode and wireless communication chips.

The Al-GaN/GaN HFET biosensor is firstly designed based on modification of conventional Al-GaN/GaN heterostructure high electron mobility transistors [HEMTs] by substituting the metal gate electrode for biomolecule immobilization [ssDNA or ssPNA for ssDNA detection and antibody for protein detection] and the formation of a reservoir for applying solutions. B. S. Kang et al. [34] used AlGaIn/GaN heterostructures to detect DNA hybridization. They used thiolated DNA to tether the DNA molecule to the gold sputtered gate surface. 4% polymethyl methacrylate [PMMA] was used to encapsulate the device except the gate region by e-beam lithography. When the thiol functionalized DNA was exposed to the matching complementary target DNA the DNA hybridization resulted in a change in the source-drain current by 150% A. The same device structure has also been used to detect PSA46, Kidney injury molecules [35] and glucose [36] at low concentrations by functionalizing the gate surface appropriately.

A silanization and biotinylation procedure was developed to immobilize the streptavidin [SA] on the AlGaIn surface. The devices show reasonable performance prior to any optimization. With feasibility demonstrated, the device sensitivity is further improved in three aspects. Inductively coupled plasma [ICP] plasma has been found to produce the highest surface protein coverage and the best electrical properties [i.e. less surface trap density]. The second is to operate devices in the sub threshold regime. In this regime, the drain current versus the gate voltage follows a semi-log relationship. The biomolecule introduced an effective voltage shift that results in much higher current change. The results with sub threshold regime operation have shown a sensitivity improvement of seven orders of magnitude. The third method is to recess the AlGaIn barrier so that a much smaller gate voltage is necessary to bias the device at the sub threshold regime. With this strategy, the noise induced by the gate current and ion movements is reduced while signal-to-noise ratio is increased. The sub threshold swing is 74.4 mV/decade, which is largely improved. The SA detection limit is lowered one order of magnitude compared to the subthreshold regime operation. To extend the application of AlGaIn/GaN protein sensors, anti monokine-induced interferon gamma [MIG] IgG is immobilized on silanized AlGaIn surfaces for MIG detection. [36-40].

The sensors have shown reasonable detection limits for clinical applications. To model and improve the device performance; a two-dimensional analysis has been developed for planar AlGaIn/GaN biosensors.

The field-effect AlGaIn/GaN HFET biosensors have been designed for the detection of proteins. [41] With the optimization of oxidization methods and operating the device in subthreshold regime, the sensitivity is largely improved. Theoretical and numerical analysis have been developed to predict and improve the device performance. Besides, EIS characterizations of tBLMs with well-defined nanopores were developed to study the cell membrane

channel opening, which can be used in drug/gene delivery applications [42].

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