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Polarization effects in nitride semiconductors and device structures

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Abstract Wide bandgap nitride semiconductors have recently attracted a great level of attention owing to their direct bandgaps in the visible to ultraviolet regions of the spectrum as emitters and detectors. Moreover, this material system with its favorable hetero-junctions and transport properties began to produce very respectable power levels in microwave amplifiers. If and when the breakdown fields achieved experimentally approach the predicted values, this material system would also be very attractive for power switching devices. In addition to the premature breakdown, high concentration of defects, and inhomogeneities, a number of scientific challenges remain including a clear experimental investigation of polarization effects. In this paper, following a succinct review of the progress that has been made, spontaneous and piezoelectric polarization effects and their impact on sample device-like hetero-structures will be treated.

Key words GaN · Semiconductor nitrides · Spontaneous polarization · Strain · Piezoelectric polarization · AlGaN heterostructures · AlGaN/GaN MODFETs

Introduction

Semiconductor nitrides such as aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) are very promising materials for their potential use in optoelectronic devices (both emitters and detectors) and high power/temperature electronic devices as have been treated in length and reviewed recently [1–5]. These materials and their ternary and quaternary alloys cover an energy bandgap range of 1.9 to 6.2 eV, suitable for band-to-band light generation with colors ranging from red (potentially) to ultraviolet (UV) wavelengths. Specifically, nitrides are suitable for such applications as surface acoustic wave devices [6], UV detectors [7, 8], Bragg reflectors [9], waveguides, UV and visible light emitting diodes (LEDs) [10–12], and laser diodes (LDs) [13] for digital data read-write applications. During the last several decades, lasers and LEDs have expanded remarkably both in terms of the range of emission wavelengths available and brightness. The nitride semiconductor-based LEDs have proven to be reliable in such applications as displays, lighting, indicator lights, advertisement, and traffic signs/signals; possible applications include use in agriculture as light sources for accelerated photosynthesis, and in health care for diagnosis and treatment. Lasers, as coherent sources, are crucial for high-density optical read and write technologies. Because the diffraction-limited optical storage density increases almost quadratically as the probe laser wavelength is reduced, nitride-based coherent sources at wavelengths down to UV are attracting a good deal of attention. Optical storage would enable the storage and retrieval of inordinate numbers of images and vast quantities of text with untold efficiency. Other equally attractive applications envisioned include printing and surgery.

When used as UV sensors in jet engines, automobiles, and furnaces (boilers), the devices would allow optimal fuel efficiency and control of effluents for a cleaner environment. Moreover, UV sensors that operate in the solar blind region (260 to 290 nm) would have high detectivity because the ozone layer absorbs solar radiation at those wavelengths, thus virtually eliminating radiation noise. Consequently, these detectors are expected to play a pivotal role in threat recognition aimed against aircraft [7, 8, 14]. GaN/AlGaN UV *p-i-n* detectors have demonstrated sensitivities of about 0.12 A/W and response speed of a few nanoseconds in 250 μm dot sizes; both values represent a quantum leap over previous capability.

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GaN's large bandgap, large dielectric breakdown field, fortuitously good electron transport properties, and good thermal conductivity are conducive for use in high power electronic devices [15]. Sheppard et al. [16] already reported that 0.45 μm gate high power modulation doped FETs (MODFETs) on SiC substrates exhibit a record power performance. The power density of 6.8 W/mm in a 125 μm-wide device and a record total power of 4 W (with a power density of 2 W/mm) at 10 GHz were reported. Other groups have also reported on the superior performance of GaN-based MODFETs on SiC and sapphire substrates with respect to competing materials, particularly at X band and higher frequencies [16–19]. Applications include amplifiers operative at high temperatures and in unfriendly environments as well as in low-cost compact amplifiers for earthbound and space applications.

Nitride semiconductors have been deposited by vapor phase epitaxy (i.e., both hydride VPE [HVPE] and organometallic VPE [OVPE]), and in a vacuum by molecular beam epitaxy (MBE). With its innate refined control of growth parameters, *in-situ* monitoring capability, and uniformity, MBE is well suited for depositing heterostructures and gaining insight to deposition/incorporation mechanisms. MBE's control over growth parameters is such that any structure can be grown in any sequence. The structures for IR lasers in CD players, surface emitting vertical cavity lasers, and high-performance electronic devices such as pseudomorphic MODFETs have all been produced very successfully, all of them commercially, by MBE. Nitride growth, however, requires much higher temperatures than those used in producing the conventional group III-V semiconductors for which the MBE systems were designed. In addition, it has proved difficult to provide active N species at sufficiently high rates for nitride growth. Despite these mechanical/engineering limitations and its relatively late entry, MBE has already played a key role on a number of fronts, such as high performance GaN-based MODFETs and fast solar blind detectors that have been discussed elsewhere [14].

Being non-centro-symmetric, nitrides exhibit large piezoelectric effects when under stress along the c-direction. What is not as appreciated is the spontaneous polarization at hetero-interfaces caused, in an over simplistic view, by the ionicity and uniaxial nature of the wurtzite structure. Polarization causes a sizable red shift (Stark Effect) [20] in transition energies in InGaN/GaN [21, 22] and AlGaN/GaN [20, 23–25] quantum wells. Polarization and pyroelectric effects due to hetero-interfaces in an ionic crystal, misfit and thermal strain, anisotropy, and temperature gradients have important ramifications in electronic devices, particularly in modulation doped FETs. For example, electric field caused by polarization effects can increase or decrease interfacial free carrier concentrations. As in the case of quantum wells, the literature interpretation of polarization effects in devices has so far been lumped into piezoelectric effects [26–27].

Despite highly imperfect material, device performance in both emitters/detectors, and the microwave amplifiers has been truly outstanding. If the defects causing premature breakdown were reduced/eliminated, one would wonder whether it would be wrong at all to attempt to develop power/switching devices with large hold voltages and current handling capabilities. In this paper the topical topic of polarization issues will be visited.

Polarization effects

As alluded to earlier, observations support the presence of electric field in GaN-based heterostructures. The genesis is two fold: piezoelectric effects and the difference in spontaneous polarization between AlGaN and GaN even in the absence of strain. Spontaneous polarization was only recently fully understood, see King-Smith and Vanderbilt [28], Resta [29], and Bernardini and Fiorentini [30]. Nitrides lack inversion symmetry and exhibit piezoelectric effects when strained along [0001]. Piezoelectric coefficients are almost an order of magnitude larger than in traditional III-V, see Ref. [31], as shown in Table 1. In addition, wurtzite GaN has a unique axis, thus allowing spontaneous polarization (P_0 whose values are given in Table 1) even in the absence of strain. This manifests itself as polarization charge at hetero-interfaces. Caution must be exercised here as polarization effects assume insulating films. Defect laden GaN and related materials with large concentrations of free carriers hardly qualify for the simple picture that is about to be discussed. A particular concern involves the spontaneous polarization in that sharp and ideal interfaces with a textbook case atomic arrangement are required for the simple description to apply. Nevertheless, it is very instructive to go through the processes involved, albeit in ideal cases.

Polarization is dependent on the polarity of the crystal, namely whether the bonds along the c-direction are from cation sites to anion sites or visa versa. The convention is that the [0001] axis points from the face of N plane to the Ga plane and is the positive z-direction. In other words, when the bonds along the c-direction (single bonds) are from cation (Ga) to anion (N), the polarity is said to be Ga polarity. In this case the direction of the

Table 1 Piezoelectric Constants and Spontaneous Polarization Charge in Nitride Semiconductors

	AlN	GaN	InN
e_{33}* [C/m²**]	1.46	0.73	0.97
e_{31}* [C/m²]	–0.60	–0.49	–0.57
$\mathbf{P_0}$ [C/m²]	–0.081	–0.029	–0.032
[e_{31}–[C_{31}/C_{33}***]e_{33}]	–0.86	–0.68	–0.90

* e_{31} and e_{33} are piezoelectric constants
** C/m² is coulombs per square meter
*** C_{31} and C_{33} are elastic constants
Note that these are all in C/ m² and that 1 C/m²= $6.25*10^{14}$ e/cm²

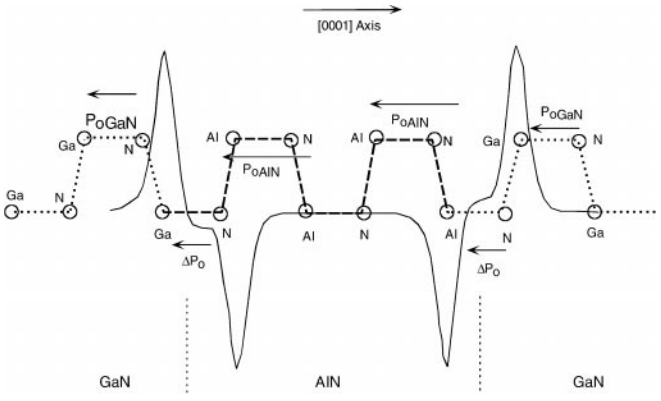

Fig. 1 Spontaneous polarization at AlN/GaN interfaces in a hetero-structure with Ga-polarity, i.e., the c-direction bonds point from Ga to N sites. The surface also represents the Ga layer

bonds are from Ga to N along the c-direction and the direction is said to be [0001] direction which is the + z direction as shown in Fig. 1. By the same argument, when the bonds along the c-direction (single bonds) are from anion (N) to cation (Ga), the polarity is said to be N polarity. In this case the direction of the bonds are from Ga to N along the c-direction, and this particular direction is said to be [000$\bar{1}$] direction which is the – z direction. To shed further light, the Ga polarity means that if one were to cut the perfect solid along the c-plane where one breaks only one bond, one would end up with a Ga terminated surface.

Let us compare the relative importance of spontaneous polarization to piezoelectric polarization.

For a biaxially strained layer the effective piezoelectric polarization is given by

$$P_z^{piezo}=[e_{31}-(C_{31}/C_{33})e_{33}]\varepsilon_{\perp} \quad (1)$$

where $\varepsilon_{\perp}=\varepsilon_{xx}+\varepsilon_{yy}$ is the in-plane strain and C_{31} and C_{33} are elastic constants. The numerical values for $[e_{31}-(C_{31}/C_{33})e_{33}]$ are listed in Table 1 using the values for elastic constants from Kim et al.[32] and piezoelectric and spontaneous polarization data from Bernardini et al.

For coherently strained $Al_xGa_{1-x}N$ on a relaxed GaN substrate (buffer layer), the strain $\varepsilon_{\perp}$ is expected to be proportional to x. It is tensile and given by $\varepsilon_{\perp}=2x(a_{GaN}-a_{AlGaN})/a_{AlGaN.}$ In our case the amplitude of the strain reduces to 0.0495*x* (using 3.112 Å for AlN c-plane lattice constant and 3.189 Å for GaN c-plane lattice constant, (here *x* is in the range of 0–1 and depicts the AlN mole fraction in the alloy). The piezoelectric polarization is then $P^{piezo}=-4.26x*10^{-2}$ C /cm^2 or $2.66x*10^{13}$ e/cm^2 and points in the [000$\bar{1}$]direction. The corresponding difference in spontaneous polarization between $Al_xGa_{1-x}N$ and GaN is also expected to be proportional to x and is given by $\Delta P^{spon}=-0.052x$ (C/m^2) or $3.25x*10^{13}$ e /cm^2. Note that the two polarization effects have the same sign for Ga polarity and tensile strain in the alloy, and point in the [000$\bar{1}$] direction.

For an $In_xGa_{1-x}N$ layer, the situation is rather different in that the differential spontaneous polarization between $In_xGa_{1-x}N$ and GaN is much smaller, $\Delta P^{spon}=-0.003x$ which translates to $1.88x*10^{12}$ e /cm^2. Furthermore, the $In_xGa_{1-x}N$ layer on GaN would be under compressive strain. The amplitude of the in plane strain is $\varepsilon_{\perp}=-0.195x$ if 3.533Å and 3.189 Å for c-plane lattice constants for InN and GaN are used. Here *x* is in the range of 0 –1 and depicts the InN mole fraction, and $P^{piezo}=+0.176x$ or $1.1x*10^{14}$ e/cm^2. For an InN mole fraction of 0.15, $P^{piezo}=1.65*10^{13}$ e/cm^2. In this particular case, the piezoelectric polarization dominates and is opposite in direction to spontaneous polarization and even larger in absolute magnitude.

In the AlGaN case, the sign of the PE polarization is such as to produce a potential energy for electrons sloping down from the Ga face towards the N face. Thus, for a structure in which the Ga face is turned towards the surface, the potential will slope down from the AlGaN surface towards the AlGaN/GaN interface and helps to drive electrons towards the two-dimensional electron gas (2DEG) forming at this interface. For example, if there is an ohmic metal contact on the AlGaN surface, electrons will flow towards the 2DEG below that layer. Consequently, for a structure with Ga polarity, the potential will slope down from the AlGaN surface towards the AlGaN/GaN interface. This potential gradient will help to drive free electrons towards the interface forming a 2DEG. In presence of an ohmic metal contact on the AlGaN surface, electrons will flow from the contact towards the 2DEG below that layer.

The most favorable situation for enhancing sheet carrier concentration would occur for an InGaN (under compressive strain) quantum well on top of a relaxed n-GaN and below an AlGaN barrier (under tensile strain) with the entire structure having cation (Ga) polarity. In that case, the field will slope down towards the InGaN/AlGaN interface in the quantum well and will help localize the electrons in the 2DEG. Note that the piezoelectric polarizations estimated here are based on the theoretical values for perfectly insulating materials. The polarization induced field will be screened by the carriers present in each layer. For example, if carriers flow from a metal contact towards the 2DEG, then this will set up a counteracting field. The equilibrium self-consistent field is ultimately determined by the requirement that the chemical potential for electrons (i.e. the Fermi level) must be constant throughout the structure and thus depends on the doping and band bending in the substrate and possibly in each of the layers. At the very least, one may expect these fields will be reduced by a factor corresponding to the macroscopic dielectric constant, i.e. a factor of order 10 but possibly larger if the layers acquire conductivity by free carriers. Consequently, a more realistic expectation for the effects on sheet carrier concentration is of the order of 10^{11}–10^{12} e/cm^2.

The difference between these and traditional device structures without polarization effects is that for uniform doping concentrations, one obtains parabolically varying potentials with distance. Here, the linear terms from the polarization must be added on top of the parabolic terms. These linear terms lead to variations of the potential over

a shorter distance scale determined by the thickness of the layers, while the parabolic terms correspond to the space-charge regions. Thus the linear terms may help to localize carriers if the polarity of the structure is chosen properly.

Some further words of caution about the above estimates are needed. If the AlGaN layers are not pseudomorphic but partially relaxed (by misfit dislocations for example), then the piezoelectric effect would be reduced but the spontaneous polarization would not. If the interfaces are not atomically sharp but exhibit a certain degree of interdiffusion then the differences in spontaneous polarization would be reduced as well if such grading occurs over a large thickness. Finally, if domains with inverted polarity exist then the overall polarization effects may be washed out. Also note that in a inverted structure with N polarity towards the surface, it may be possible to create a 2DHG (hole-gas) at the AlGaN/substrate GaN interface, but if a n-type GaN layer is placed on top, a 2DEG may form on top of the AlGaN layer.

There is another effect with its genesis in the polarization effect. This is the pyroelectric effect with important implications in devices. Anisotropy in wide bandgap semiconductors is expected to cause thermal stimulus and thermal gradients. The latter is quite likely in devices where the junction temperatures are high against a relatively cool bulk. In such a case, the thermally induced electric field, pyroelectric effect, would be present with effects similar to those described above. This phenomenon has not been studied in detail in nitride semiconductors. Contrary to this lack of attention, the electric field generated by thermal gradients, occurs readily in power devices, is comparable to the fields caused by applied voltages in nitride based FET like devices.

The immediate impact of this polarization is that the field generated by this process must be considered together with that induced by the applied voltage and charge redistribution. Moreover, as alluded to earlier, free carriers can also be drawn from any shallow and weakly bound impurities and metal in contact with the semiconductor. In any case, the free carriers would tend to screen the piezoelectric-induced polarization field. An additional complicating factor in nitrides in relation to polarization is that the semiconductor tends to twist and tilt in a columnar fashion, in an effort to minimize strain as shown in Fig. 2. These columns do not necessarily have the same cation/anion ordering polarity as shown in Fig. 2. In the presence of strain, Ga polarity domains and N polarity domains would have opposite polarization, causing increased scattering.

Figure 3 is a schematic representation of an ideal inversion domain boundary formed in growth along the [0001] direction. On the left of the boundary, the growth initiates with N, and on the right it begins with Ga. On the left side, the bond along the [0001] direction is from Ga to N; this is called Ga polarity. On the right side, the [0001] bonds are from N to Ga; this is called N polarity. In N polarity and under tensile strain, the PE field generated points toward the surface, whereas that for the Ga polarity region points in from the surface. When the strain is compressive, the direction of the field changes. Yet an additional complicating factor is the asymmetry in the barrier discontinuities between GaN and its binary and ternaries caused by spontaneous polarization [30]. The spontaneous polarization arises simply because of the ionicity of the bonds and the low symmetry in wurtzite structures. In fact, Bernardini et al. [31] showed that the field that occurs in quantum wells is almost completely determined by both the differential spontaneous polarization between the two semiconductors, and their PE contribution. The field (i.e., the slope of the potential) is quite independent of the offset (i.e., the dipole discontinuity that occurs at the interface between the two materials). In other words, the dipole at the interface appears independent from the charge (monopole) accumulated at the interface.

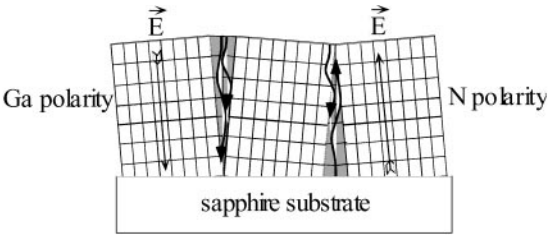

Fig. 2 Domains in GaN, with N polarity (nitrogen surface layer) on the right and Ga polarity (with Ga on surface) on the left side under compressive residual strain. The arrows show the direction of the piezoelectric field in each of the domains (patterned after a figure provided by Prof. S. Hersee)

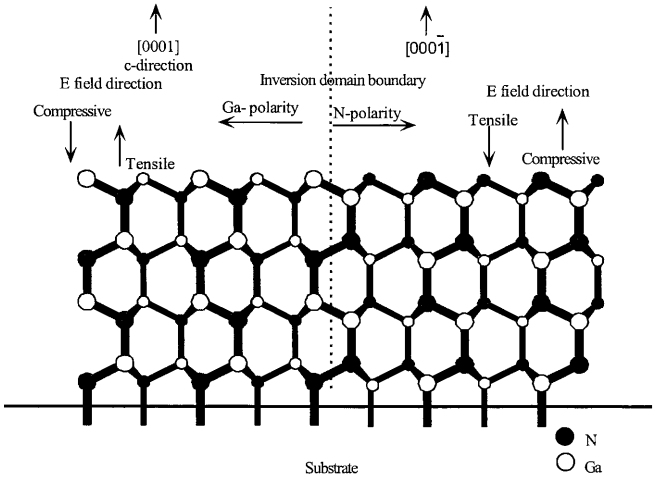

Fig. 3 Schematic representation of an ideal inversion domain boundary formed along the c-axis

Polarization in device-like structures

Polarization effects and devices are inextricable. In devices with large concentration of free carriers, the polarization charge would be screened. One such device is the MOdulation Doped Field Effect Transistor (MODFET) [33], the GaAs version of which dominates the high fre-

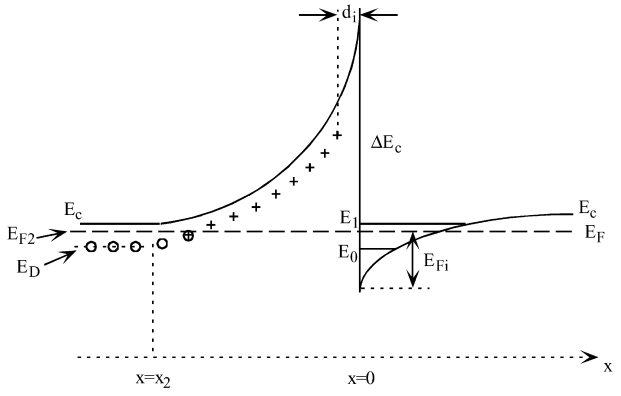

Fig. 4 Conduction band structure of a modulation-doped structure

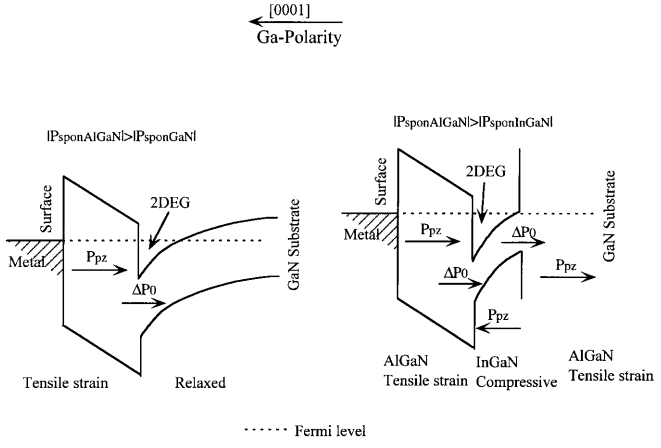

Fig. 5 GaN based normal modulation doped structures with Ga polarity and GaN and InGaN active layers. If the sign of strain were to change, to compressive from tensile, then the direction of the piezoelectric polarization would change. In that case the spontaneous and piezoelectric polarization charges would oppose one another, and the larger one would determine whether hole or electron accumulation is favored at the interface

quency, low noise, and high power (at high frequencies) device market. Recently, this device structure has been extended to include the GaN varieties. A schematic representation of a GaN/AlGaN heterostrucure used for MODFETs is shown in Fig. 4. In considering a Normal MODFET (N-MODFET) structure where the larger bandgap AlGaN donor layer is deposited on top of a GaN channel layer, see Fig. 5, both the spontaneous polarization and piezoelectric polarization must be accounted for. For an N-MODFET structure with Ga polarity, the potential will slope down from the surface of the AlGaN layer towards the AlGaN/GaN interface and will help to drive free electrons towards the interface forming a 2DEG as shown in Fig. 5. For example, if there is an ohmic metal contact on the AlGaN surface, electrons will flow towards the 2DEG below the AlGaN layer from contacts. Since nitride semiconductors in question have large bandgaps, thermal generation rates are minuscule and the role played by thermally generated carriers can be ignored even at growth temperatures.

The most favorable situation for enhancing sheet carrier concentration would occur for an InGaN (under compressive strain) quantum well on top of a relaxed n-GaN and below an AlGaN barrier (under tensile strain) with the entire structure having cation (Ga) polarity as shown on the right side in Fig. 5. In that case, the field will slope down towards the InGaN/AlGaN interface in the quantum well and will help localize the carriers in the 2DEG. Note that the piezoelectric polarization vectors estimated here are based on the theoretical values for perfectly insulating materials. Since the structures available are not perfectly insulating, the field is screened by the carriers present in each layer. For example, if carriers flow from a metal contact towards the 2DEG, then this will set up a counteracting field. The equilibrium self-consistent field is ultimately determined by the requirement that the chemical potential for electrons (i.e. the Fermi level) must be constant throughout the structure and thus depends on the doping and band bending in the substrate and possibly in each of the layers. At the very least, one may expect these fields will be reduced by a factor corresponding to the macroscopic dielectric constant, i.e. a factor of order 10, even possibly larger if the layers acquire conductivity by free carriers. Consequently, a more realistic expectation for the effects on sheet carrier concentration is of the order of 10^{11}–10^{12} e/cm^2. A fully consistent solution of the Poisson's equation must be found with the spontaneous polarization component as interface charge in order to get the accurate charge distribution.

A case of importance in GaN based semiconductors is the polarity of the epitaxial layer, i.e., whether the Ga or the N plane forms the surface. It is therefore essential that the N-face case also be considered. The case of an AlGaN (tensile strained) /GaN (relaxed) heterostructure with nitrogen polarity for an n-type GaN and for a p-type GaN buffer layers is shown for an in Fig. 6. As in the cases depicted in Fig. 5 where the piezoelectric polarization and spontaneous polarization charges support one another. Unlike the Ga-polarity case, the polarization charge is such that screening charge will be made of holes if they are present in the film. If holes constitute the minority charge in the film, then the thermal process is the means by which they would be created. However, this process in a wide bandgap semiconductor such as GaN is very slow and equilibrium condition may not be attained. If the strain in AlGaN were compressive, the direction of the piezoelectric polarization vector would change causing the piezoelectric polarization to counter the spontaneous polarization. This would actually represent the case when the epitaxial films are relaxed at the growth temperature and upon cooling to room temperature, the film would be under compressive strain if on sapphire substrates. This is due to the expansion coefficient of sapphire being larger than that of GaN. In such a case, the larger of the two would dominate and determines whether hole or electron accumulation would be favored. If on the other hand the film is grown on SiC substrates, the strain due to thermal expansion would be

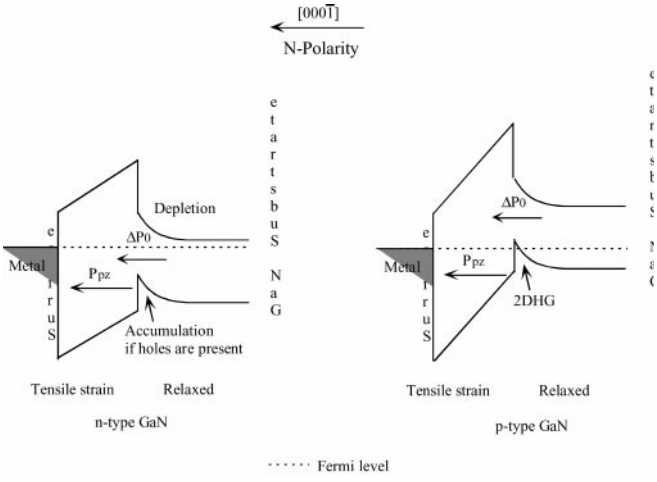

Fig. 6 AlGaN/GaN based normal modulation doped structures with N polarity with two cases, one for n-type and the other for p-type buffer layer. If the sign of strain were to change, to compressive from tensile, then the direction of the piezoelectric polarization would change. In that case the spontaneous and piezoelectric polarization charges would oppose one another, and the larger one would determine whether hole or electron accumulation is favored at the interface

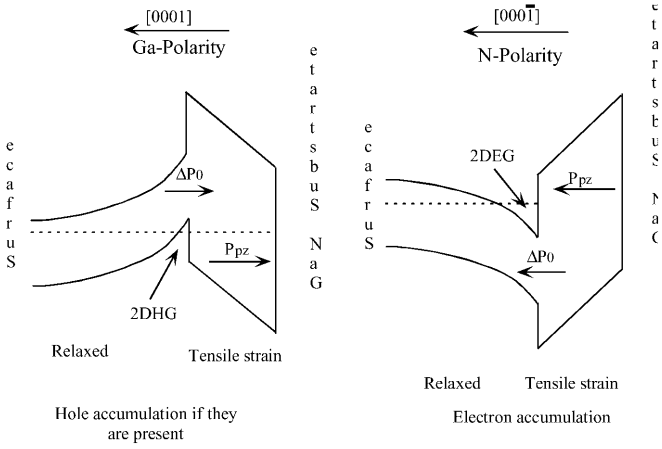

Fig. 7 AlGaN/GaN based Inverted modulation doped structures with Ga, and N-polarity. As can be seen, in the case of Ga polarity and tensile strain in AlGaN, both the piezoelectric and spontaneous polarization vectors support each other leading to hole accumulation at the interface if holes are present in the system. The other source, thermal generation rate is very small and the semiconductor structure can not be expected to reach equilibrium by this means at room temperature in a reasonable period of time. On the other hand, with N-polarity and tensile strain in AlGaN, the structure favors electron accumulation at the interface. If the sign of strain were to change, to compressive from tensile, then the direction of the piezoelectric polarization would change. In that case the spontaneous polarization and piezoelectric polarization would oppose one another, and the larger one would determine whether hole or electron accumulation is favored at the interface

tensile. This would lead to the case where the piezoelectric polarization and spontaneous polarization would support one another.

Inverted modulation doped structures can also be used to interrogate the picture in effect and perhaps take advantage of the unique features present. In such a case, the AlGaN layer precedes the GaN top layer where the charge accumulation would occur. The interface between the AlGaN layer and the bottom GaN layer which is referred to as the buffer layer would be graded to avoid a normal interface from forming.

Figure 7 shows an AlGaN/GaN based inverted modulation doped structures with Ga, and N-polarities. As can be seen, in the case of Ga-polarity and tensile strain in AlGaN, both the piezoelectric and spontaneous polarization vectors support each other leading to hole accumulation at the interface if holes are present in the system. Since the thermal generation rate is very small, the semiconductor structure can not be expected to reach equilibrium by this means at room temperature in a reasonable period of time. On the other hand, with N-polarity and tensile strain in AlGaN, the structure favors electron accumulation at the interface. If the sign of strain were to change, to compressive from tensile, then the direction of the piezoelectric polarization would change. In that case the spontaneous and piezoelectric polarization charges would oppose one another, and the larger one would determine whether hole or electron accumulation is favored at the interface.

The physics literature appears to be fairly clear in that the polarization charge is a bound charge and that any free carriers act only to screen it. However, the device reports on GaN FETs have gone so far as to suggest that piezoelectric effect in and of itself is sufficient to provide the free carriers needed for devices. More over, polarization effects, particularly spontaneous polarization have immense impact on measured band discontinuities. For example, the dependence of measured band discontinuities on the order in which the larger and smaller band gap semiconductors are grown, is one that can be attributed to polarization effects [34–36]. The complicating factor in nitrides is the lack of polarity control, Ga or N polarity, and lack of uniform polarity meaning presence of inversion domains.

To reiterate, as a result of polarization, the static potential at the GaN/AlN interface is different from that at the AlN/GaN interface that gives rise to interface charge larger than the charge densities used in devices. A substantial level of effort has been expended toward determining band discontinuities, but the field is in desperate need of more in depth investigations in improved structures. The observed asymmetry in AlN/GaN and GaN/AlN interfaces caused by spontaneous polarization is within the experimental errors of Martin et al [35–37]. Inversion domains, see Fig. 3, combined with any strain in semiconductor nitrides lead to flipping PE fields, see Fig. 2, with adverse effects on our ability to characterize the films, let alone exploit this phenomenon for devices. Such flipping field would also cause increased scattering of carrier as they traverse in the c-plane. Simply put, identical device structures with different polarity layers would have widely differing performance underscoring the importance that these issues will have to be investi-

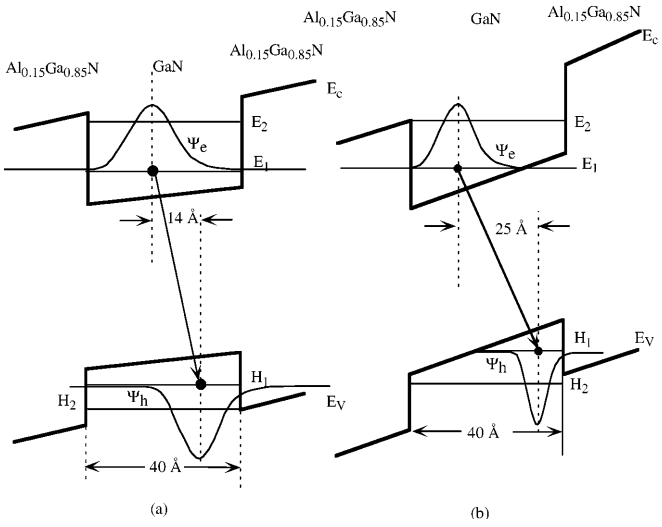

Fig. 8a, b The effect of the field where (**a**) depicts the case, e.g., shortly after the excitation pulse with large numbers of excess carriers. The case (**b**) depicts the evolution of the band structure some time later as the excess carriers are allowed to recombine

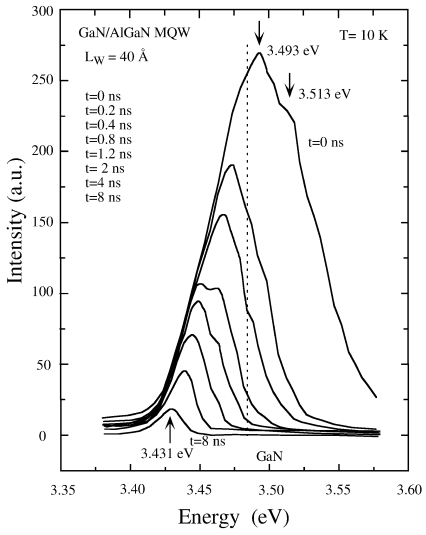

Fig. 9 Time resolved PL signal from a 40 Å well AlGaN/GaN MQW structure grown by MBE

gated and reconciled. The polarity mixing causes the PE induced electric field to flip from one domain to the next, causing a variation in the sheet carrier concentration along the channel of an FET like device. The same polarity mixing would have deleterious effects in the base of an HBT as well and depending on the polarity the induced field would either aid or impede minority carrier transit.

Effect of polarization in quantum wells

Polarization effects manifest themselves in quantum wells as Stark effect as shown in Fig. 8. Time resolved photoluminescence [23] measurements performed in GaN/AlGaN MQWs indicated that temporal evolution of the A exciton peak undergoes a red shift as the recombination depletes the excess carriers as shown in Fig. 9. If one assumes that the red shift is due to polarization induced field, one can determine the intensity of the field. To a first extent the linear approximation, that is constant electric field, can be used. For thicker quantum wells, the quadratic approach would be more accurate. The picture may be more complex and suffer from variations in samples as blue shift too has been observed which may have to do with inter-well excitons and oblique excitons [37]. Though controversial, in lasers the injected carrier concentrations, even at transparency, are comparable to polarization induced charge, 10^{13} cm^{-2}, which means that the PE induced field is screened. However, the PE effect reduces the gain at lower injection levels due to, among others, reduced oscillator strength.

Using optical transitions in GaN/AlGaN, the authors and their colleagues [25] have revisited the physical origin of the built-in field and its effect on quantum wells. The results suggest that the built-in field, at least in the samples investigated, originates primarily from the spontaneous polarization charge formed at the GaN/AlGaN interfaces, with a minor contribution from the piezoelectric field induced by strain (lattice mismatch and thermal strain or both). Such a built-in electric field causes:

(i) A band bending and a red-shift of the gap which largely overcome the blue-shift expected from the quantum size effect.

(ii) S progressive separation of the electron and hole wave-functions with increasing the well width, resulting in the decrease of the emission strength and in the increase of the decay times.

The experiments reveal that the fundamental transition of the quantum wells occurs at an energy that is *well* below the bulk GaN gap for well widths larger than 3 nm (for the specific case of GaN/ $Al_{0.15}Ga_{0.85}N$). A total built in field of the order of a few MV/cm is found and used to explain qualitatively the optical data. Moreover, a quantitative description of the red-shift and oscillator strength are obtained by means of a self-consistent tight-binding (TB) model which specifically accounts for the total built-in field and for the screening, either dielectric or induced by the photo-generated carriers. The impact of the built-in field on the actual electrostatic stability of the exciton quasi-particle in GaN quantum wells is also addressed.

One and two-photon absorption photoluminescence spectroscopy methods have been applied to investigate $GaN/Al_{0.15}Ga_{0.85}N$ quantum wells of increasing thickness. The samples were grown by reactive molecular beam epitaxy on sapphire substrates. Following a chemical and in situ cleaning of c-plane sapphire substrates, a thin AlN buffer layer was grown at 850°C with ammonia as the active nitrogen source. This was followed by the growth of a 1 μm thick GaN buffer layer grown at

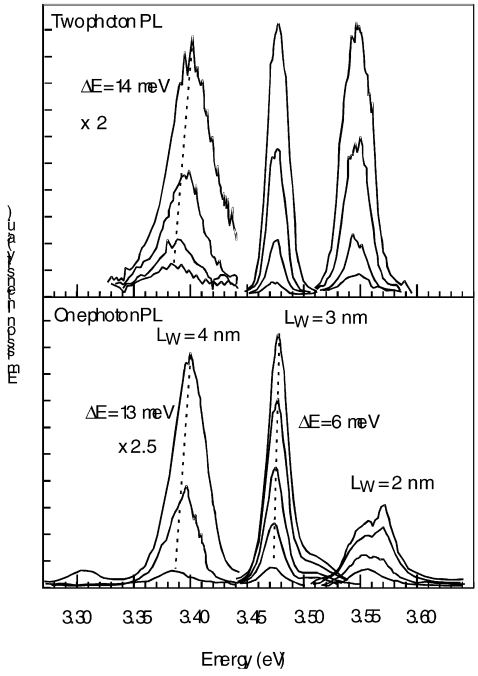

Fig. 10 One and two photon luminescence for 2, 3, and 4 nm GaN/AlGaN quantum wells with injection level as the parameter

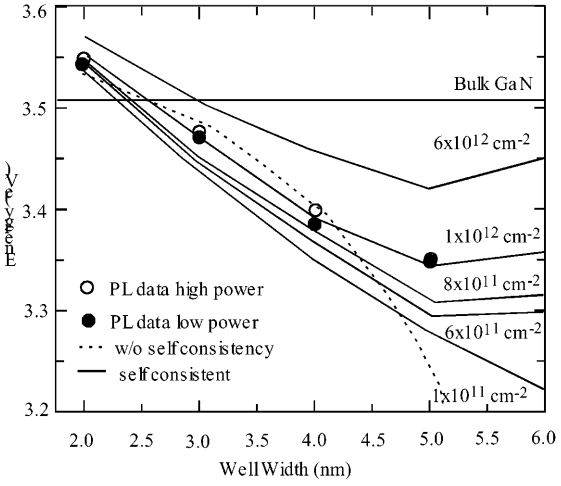

Fig. 11 The transition energies in GaN/AlGaN quantum wells as a function of well thickness. The solid and open circles indicate results with lower and higher power, respectively. Calculated values for the indicated injection levels are also shown with very good agreement with experiments

800°C. Finally, the quantum well region was grown. Each sample consisted of 10 GaN quantum wells. Five samples of well widths L_w=2 nm, 3 nm, 4 nm 5 nm, 9 nm, were grown and analyzed. The barrier width and composition were kept constant in all samples ($Al_{0.15}Ga_{0.85}N$ barriers of thickness L_b=10 nm).

Linear luminescence was excited either by the 325 nm line of a cw He-Cd laser (10 mW power) or by the 337.1 nm line of a pulsed N_2 laser (300 kW peak power), in order to study the density dependent screening of the built-in field generated by the photo-generated carriers. Two-photon absorption induced luminescence was also measured in order to make sure that the observed blue-shift was not due to band-filling of hot electron-hole pairs, and to avoid the undesired occurrence of localized-states and impurity related emission in the spectra. In these experiments, the half-gap excitation provided by the tunable output of a pulsed parametric oscillator, was tuned at the fundamental n=1 electron-heavy-hole resonance ($2\hbar\omega=E_{1e1h}$) of the quantum well. Time resolved luminescence was also measured by using the third harmonic of a pico-second Ti:Sapphire laser and a streak-camera. All measurements were performed at 10 K.

In Fig. 10, we display a few representative PL spectra recorded at 10 K under one- and two-photon absorption excitation and for different power densities. First of all we note that the quantum well emission is dominant and no barrier luminescence or impurity related emission is observed under pulsed excitation. The emission energy decreases with increasing well width, as expected from the quantum size effect. However, we note that for large well widths the E_{1e1h} transition falls *below* the bulk GaN gap (3.51 eV at 10 K). In order to eliminate possible extrinsic recombination processes, we have performed two-photon absorption experiments with approximately half-gap excitation ($2\hbar\omega=E_{1e1h}$). Both the linear and nonlinear spectra exhibit the same energy positions and linewidths for the quantum well structures under investigation, indicating that carrier heating or any possible extrinsic effects do not influence the luminescence spectra of these samples. Furthermore, we note that all samples exhibit a substantial blue-shift with increasing photogeneration rate, under both one- and two-photon absorption excitation. This suggests a screening induced blue shift caused by the partial compensation of the Stark effect by the photo-generated carriers. It is important to mention that the emission spectra do not show any significant intensity dependence under low-power cw excitation, suggesting that at low photo-generation rates the screening of the built-in field is negligible and is of no consequence.

In Fig. 11, we display the progressive reduction of the emission efficiency and the increase of the decay times occurring with increasing well width. In an effort to shed light on the polarization issue, the total polarization charge can be written as $P_{tot}= P_{piezo}+P_{spont,}$ where P_{piezo} is the piezoelectric charge caused by the lattice mismatch (lm) strain and by the thermal strain (ts) [$P_{piezo} = P_{lm}+P_{ts}$], whereas P_{spont} represents from the spontaneous polarizability of the GaN/AlGaN interface, as clearly demonstrated by the recent works of Bernardini et al. [30, 31].

The aforementioned experimental results support the argument that the built-in field originates primarily from the spontaneous polarization charge formed at the GaN/AlGaN interfaces with a minor contribution from the piezoelectric field induced by strain (either lattice mismatch and thermal strain) as has been predicted. The

experimental data, shown in Figs. 9–10, reveal that the fundamental transition of the quantum wells occurs at an energy that is *well* below the bulk GaN gap for well widths larger than 3 nm (for the specific case of $GaN/Al_{0.15}Ga_{0.85}N$). Care was taken to assure that the transitions observed are of intrinsic origin by performing two-photon absorption experiments. Calculated transition energies with corresponding carrier densities depicting the blue shift caused by screening are also shown. The dotted line indicates the analytical calculations whereas the others represent self-consistent calculations.

As recently demonstrated by the works of Bernardini et al. For an alternating sequence of wells (w) and barriers (b) the total electric field in the well can be calculated as

$$F_w=-4\pi L_b(P^w_{tot}-P^b_{tot}) / (L_w\varepsilon_b+L_b\varepsilon_w)$$
$$F_b=-4\pi L_w(P^b_{tot}-P^w_{tot}) / (L_b\varepsilon_w+L_w\varepsilon_b) \quad (2)$$

Where $\varepsilon_{b,w}$ are the dielectric constants of the well and barrier layers. The piezoelectric charge induced by the in-plane lattice mismatch can be found from Eq. 1 using the in-plane strain for AlGaN/GaN as $\varepsilon_\perp=2x(a_{GaN}-a_{AlGaN})/a_{AlGaN}$ where the AlGaN is pseudomorphically strained on a relaxed GaN substrate. Thick GaN buffer layers ensures that the GaN quantum wells are not under misfit strain. Moreover, since the $Al_{0.15}Ga_{0.85}N$ layers are thin and grow pseudomorphically, they undergo a tensile in-plane strain $\varepsilon_\perp=0.742\%$. This results in a piezoelectric polarization charge $P^w_{lm}=0$ in the wells and $P^b_{lm}=-3.99 *10^{12}$ ecm^{-2} in the $Al_{0.15}Ga_{0.85}N$ barriers. The thermal strain amounts to some 0.03%, resulting in an additional polarization charge of the order of $P^w_{ts}=+2.57* 10^{11}$ ecm^{-2}. For spontaneous polarization, we take the recent data of Bernardini et al. leading to $P^w_{sp}=-1.81* 10^{12}$ ecm^{-2} and $P^b_{sp}=-7.64 *10^{12}$ ecm^{-2}, the latter value being obtained by linear interpolation of the GaN and AlN values ($P_{sp}=-5.09 *10^{13}$ ecm^{-2} in AlN). The differential-spontaneous-polarization between the $Al_{0.15}Ga_{0.85}N$ barrier, and the GaN well is then $-5.83 *10^{12}$ ecm^{-2}. By using these data and Eq. (2), one can calculate the built-in field in the different samples, which turns out to vary in the range 1–3 MV/cm depending on the actual well width. Neglecting high-field effects and corrections for self-consistency, the red-shift caused by the built-in field in the wells is given by the quadratic Stark effect [38, 39].

The measured ground level transition energies and those calculated in the square well approximation with inclusion of the Stark shift are in very good agreement. The agreement between theoretical and experimental data is very reasonable, especially if we take into account that the nominal growth parameters were used in the calculations without any fitting parameter.

The agreement between the calculated and measured data can in fact be substantially improved by the use of a self-consistent tight-binding (TB) model [40]. The tight-binding model is used to describe the electronic structure in the entire Brillouin zone, up to several eV above the fundamental gap, thus overcoming the well-known limitations of the envelope function approach. For the specific case of nitride semiconductors, the parameters of our empirical TB model were determined by fitting the band-structure of ref. [41]. For the self-consistent calculations the electron and hole quasi-Fermi levels are calculated for a given photo-injected charge density. The resulting electron and hole distribution functions (*n* and *p*, respectively) are used to solve the Poisson equation. The Poisson equation is solved assuming zero-field at the boundaries. The obtained potential is thus inserted into the TB Schroedinger equation that is solved to get the energies and wave-functions. The new quasi-Fermi levels are thus recalculated and the procedure is iterated until self-consistency is achieved. The agreement between the self-consistent calculations and the experimental data is very good both in terms of the trend and absolute values.

In conclusions, GaN and related materials exhibit optical and transport characteristics that are very well suited for visible opto-electronic devices and electronic devices (relying on electron transport). This is evident by successful LEDs and lasers, and the recent high power MODFETs with record power performance which supplanted all the other competing semiconductors at microwave frequencies. Recent theoretical and experimental investigations indicate that polarization induced charge is important in nitride semiconductors with device implications and that spontaneous polarization is dominant in many cases over the strain induced piezoelectric polarization in typical GaN/AlGaN structures. This dominance would increase if the AlGaN grown on GaN relaxes in full or in part. However, the differential spontaneous polarization between GaN and InN is much smaller than that of GaN/AlN interfaces. Assuming that the InGaN on GaN is fully strained, the piezoelectric component of polarization would dominate. Full or partial relaxation of InGaN on GaN due to defects and inhomogeities, such as compositional fluctuations, would reduce this piezoelectric polarization substantially. For now, optical transitions investigated in GaN/AlGaN quantum wells support the assertion that spontaneous polarization is dominant in those structures and must not be lumped with piezoelectric polarization.

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