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The complex impact of silicon and oxygen on the n-type conductivity of high-Al-content AlGaN

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Issues of major relevance to the n-type conductivity of Al0.77Ga0.23N associated with Si and O incorporation, their shallow donor or deep donor level behavior, and carrier compensation are elucidated by alloying (i) study of Si and O incorporation kinetics at high process temperature and low growth rate, and (ii) electron paramagnetic resonance measurements. The Al0.77Ga0.23N composition correlates to that Al content for which a drastic reduction of the conductivity of Al0.77Ga0.23N is commonly reported. We note the incorporation of carbon, the role of which for the transport properties of Al0.77Ga0.23N has not been widely discussed. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4800978]

Prospective deep-UV light emitting devices stemming from technologies based on AlN invariably integrate n-type high-Al-content AlxGa1−xN layers, x > 0.70. The n-type conductivity is conveniently accomplished by doping with Si introduced into the gas stream mostly as silane (SiH4)1–4 and occasionally as disilane (Si2H6).5 Doping of the well-explored AlxGa1−xAs alloys, 0 < x < 1, by Si2H6 has proven potent in many aspects especially when considering their typical growth temperature range of 500–900 °C.6 Thermodynamic and kinetic aspects of the Si incorporation in the AlxGa1−xAs alloys by implementing either SiH4 or Si2H6 dopant gases have been subjected to close investigation. It has being central to the establishment of their controllable n-type doping. Such scrutiny in the case of the high-Al-content AlxGa1−xN alloys is largely prevented by the material growth issues of accomplishing epitaxial layers of high-crystalline quality and surface morphology.

The issue of incorporation of residual impurities, most notably oxygen, has been equally crucial in advancing the understanding and performance of the high-Al-content AlxGa1−xN, as well as any Al-containing alloy in general. Ready reaction between the trimethylaluminum (TMAI) precursor and oxygen in the gas stream results in the formation of volatile Al(CH3)2CH2OH product, being potentially responsible for the incorporation of oxygen.7 The issue of residual oxygen incorporation in the Al-containing alloys is further aggravated by the fact that the maximum H2O/H2 ratio allowed—for example, over AlxGa1−xN:As surface—before oxygen incorporation occurs, is only in the order of 0.01 ppb.7

Once incorporated into the crystal lattice, the substitutional oxygen (OΔ) is a shallow donor in GaN. OΔ in AlN is commonly associated with deep levels, which affect the position of the Fermi level and counteract the electrical activity of any other donors.8,9 Alternatively, it has been suggested that oxygen incorporation does not have a negative effect in achieving n-type AlxGa1−xN (x ≈ 0.60), but rather enhances the conductivity.5 The speculated Si transition from shallow donor in GaN to a localized deep DX center in AlxGa1−xN alloys with increasing Al content is under a continuing debate following first-principle calculations of substitutional silicon (SiAl) in AlN.8,9

Issues of major relevance to the n-type conductivity of high-Al-content AlxGa1−xN alloys associated with Si and O incorporation, their shallow donor or deep donor level (DX) behavior, and carrier compensation sustain a subject of controversy and a better understanding is yet to emerge. The present study aims at incorporation kinetics study of Si and O in high-Al-content Al0.77Ga0.23N layers, especially with Si doping that can produce efficient carrier concentration. The incorporation kinetics study is allied with electron paramagnetic resonance (EPR) measurements, which are essential to distinguish any DX nature of involved point defects.10,11 The alloy composition of the studied layers correlates to that Al content for which a drastic reduction of the n-type conductivity of Al0.77Ga0.23N is commonly reported. The growth kinetics study points to the incorporation of other major impurities in the layers, namely carbon. Its role for the transport properties of high-Al-content AlxGa1−xN alloys has not been widely discussed.

The epilayer growth is performed in a horizontal-tube reactor based on the Aixtron AB VP508GFR deposition platform and on on-axis semi-insulating 4H-SiC substrates. Different aspects of the development of a highly efficient AlN-based epitaxial process,12,13 and typical performance of the system as to the AlN growth14 and the Mg-doped Al0.85Ga0.15N layers with low resistivity at room temperature15 can be found elsewhere. Following an in-situ template growth, the top AlxGa1−x:NiSi layer is grown at a typical process temperature of 1100 °C. Ammonia (NH3), TMAI, and trimethylgallium (TMGa) are the precursors introduced with a gas-flow-rate ratio of NH3/(TMAI + TMGa) of either 1560 or 640, at the same NH3 gas-flow-rate. The typical growth rate over 2 in. diameter deposition area is maintained at either ≈360 nm/h or 760 nm/h, respectively. The typical thickness of the top AlxGa1−x:NiSi layer is of ≈360 nm. The precursor used for doping is SiH4 at a gas-flow-rate ratio of SiH4/(TMAI + TMGa) in the range of 0.2–6.0 × 10−5, which determines the nominal doping level. Secondary ion mass spectrometry (SIMS) is employed to obtain the thickness and alloy composition of the AlxGa1−x:NiSi layers, and to
determine the H, C, O, and Si atomic concentrations.\textsuperscript{16} Cathodoluminescence (CL) panchromatic images from the layers are obtained in a field-emission gun scanning electron microscope with CL attachment (Leo1550 MonoCL2 system, Oxford Res. Instr.) at 5 K and 10 kV. The surface topography of the layers is obtained by atomic force microscopy (AFM) in a tapping mode (Veeco Dimension 3100 Scanning Probe Microscope). The mobility, carrier concentration, and conductivity are measured by contactless microwave-based technique (LEI 1610 Mobility Measurement System, Leightton Electronics, Inc.). More details of this type of technique can be found elsewhere.\textsuperscript{17} EPR measurements are performed on an X-band (\~9.4 GHz) Bruker E500 EPR spectrometer equipped with a continuous He flow cryostat, allowing the regulation of the sample temperature in the range of 4–295 K. For photo-excitation EPR experiments, a 200 W halogen lamp is used as an excitation source. Illumination with light of different photon energies can be realized using a single grating Jobin-Yvone monochromator and appropriate optical filters.

Given the tightness of the gas system and overall reactor assembly, the concentration of the incorporated oxygen is established to be further reduced by a factor of three by increasing the process temperature from 1000°C up to 1100°C. Such a low value of the residual concentration level of oxygen as [O] \~ 3 \times 10^{17} \, \text{cm}^{-3} in layers of Al_{0.77}Ga_{0.23}N:Si composition is attained. The positive impact of increasing the process temperature from 1000°C to 1100°C is established to be further reduced by a factor of three by increasing the process temperature from 1000°C to 1100°C. For the rest of the growth runs considered in this paper follow-

ting the twofold increase of the total gas-flow rate ratio SiH\textsubscript{4}/(TMAI + TMGa), the set of layers L1–L4 is grown at \~760 nm/h. The set of layers T1–T4 is grown at \~760 nm/h. The apparent two-fold increase of the growth rate is established by the twofold increase of the total (TMAI + TMGa) gas-flow rate while keeping the same Al composition in the gas-phase. Under the conditions of two-fold increase of the growth rate, pit-populated morphology develops already at [Si] \~ 7 \times 10^{18} \, \text{cm}^{-3} (layer T1 in terms

For the purposes of investigating the role of oxygen in the conductivity of the Al_{0.77}Ga_{0.23}N:Si layers, and at a process temperature of 1100°C, a certain leak is allowed upstream from the deposition zone. The concentration of the incorporated oxygen is enhanced by about one order of magnitude, up to the moderate level of [O] \~ 2 \times 10^{18} \, \text{cm}^{-3}. The immediate consequence of the intentional addition of water vapor to the gas stream is a certain decrease of the growth rate. It is inferred to result from the formation of non-volatile products (suggested as Al\textsubscript{2}O\textsubscript{3}, Al(OH)\textsubscript{3}) depleting the gas-phase from Al-containing species.

The focus, further on, is placed on the Al_{0.77}Ga_{0.23}N:Si layers, containing moderate oxygen concentration at the level of [O] \~ 2 \times 10^{18} \, \text{cm}^{-3}. Basically, this oxygen concentration compares with the moderate silicon concentration introduced from the intentional SiH\textsubscript{4} doping. In terms of the labels in Fig. 2, these are the layers L1 and L2. The label L2\textsuperscript{*} stands for an Al_{0.77}Ga_{0.23}N:Si layer grown under the conditions of no intentional leak reflected in its oxygen concentration of [O] \~ 3 \times 10^{17} \, \text{cm}^{-3}. Any of the three layers—L1, L2, and L2\textsuperscript{*}—yields resistivity of less than 0.05 Ω cm, which is on par with the best up-to-date reported values.\textsuperscript{4} For all layers, the electron mobility is \~80 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} in the range of carrier concentrations in the low 10\textsuperscript{18} cm\textsuperscript{-3}. It is to be noted that good transport properties are achieved for a moderate concentration level of [O] \~ 2 \times 10^{18} \, \text{cm}^{-3}. The Si concentration is in the range of [Si] \~ (2–3) \times 10^{18} \, \text{cm}^{-3}.

As the Si concentration in the layers increases, their transport properties deteriorate alongside with the surface morphology deterioration. This is evident by the appearance of pits in the respective AFM images. Pits start to form at [Si] \~ 2 \times 10^{19} \, \text{cm}^{-3} as shown in Fig. 1(b). This AFM image corresponds to the surface topography of the layer L3 in terms of the labels in Fig. 2. Figure 2 represents the Si incorporation for two sets of layers as a function of the gas-flow-rate ratio SiH\textsubscript{4}/(TMAI + TMGa). The set of layers L1–L4 is grown at \~360 nm/h. The set of layers T1–T4 is grown at \~760 nm/h. The apparent two-fold increase of the growth rate is established by the twofold increase of the total (TMAI + TMGa) gas-flow rate while keeping the same Al composition in the gas-phase. Under the conditions of two-fold increase of the growth rate, pit-populated morphology develops already at [Si] \~ 7 \times 10^{18} \, \text{cm}^{-3} (layer T1 in terms

![FIG. 1. AFM images representing the surface topography of high-Al-content Al\textsubscript{0.77}Ga\textsubscript{0.23}N layers grown at the low growth rate of \~360 nm/h, high process temperature of 1100°C and: (a) [Si] \~ 3 \times 10^{18} \, \text{cm}^{-3}; (b) [Si] \~ 2 \times 10^{19} \, \text{cm}^{-3}. Scan size of both images is 2 \times 2 \, \mu\text{m}^2. The rms value over the 2 \times 2 \, \mu\text{m}^2 scan is 0.30 nm and 0.25 nm, respectively.](image1)

![FIG. 2. Plots of silicon incorporation in two sets of high-Al-content Al\textsubscript{1-x}Ga\textsubscript{x}N (x \approx 0.77) layers. The set of layers L1-to-L4 is grown at \~360 nm/h. The set of layers T1-to-T4 is grown at \~760 nm/h. The concentration of the incorporated O is indicated for the layers L1, L2, and L2\textsuperscript{*}.](image2)
of the labels in Fig. 2). Figure 2 indicates that, for any growth rate, the Si atoms incorporation in the studied layers is inversely proportional to the input (TMAI + TMGa) gas-flow-rate. For all that, when the doping is performed at low growth rate, the same Si doping level in the Al0.77Ga0.23N alloy can be obtained for a reduced flow of SiH4 given that Si atoms substitute for atoms in the (Al, Ga) sub-lattice. This has the important consequence of obtaining high-Al-content Al0.77Ga0.23N doped layers of pit-free surface morphology and retained transport properties.

Admittedly, the formation of pits—caused by the raised Si doping level especially under the conditions of enhanced growth rate—entails high resistivity. The layer T4 in Fig. 2, grown at \( \sim 760 \text{nm/h} \) and heavily doped to \([\text{Si}] \sim 1 \times 10^{20} \text{cm}^{-3} \), represents an extreme case. The relaxation of the Si-doping-induced tensile strain creates cracks as evident from its panchromatic CL image [Fig. 3]. The purpose here is, however, to point to the observed pits of bright contrast. These pits are reminiscent of the pits discussed in relation to the kinetic effects during AlN epitaxial growth and associated with nanopipes/large pinholes. High growth rate and/or heavy Si doping can stir surface roughness, giving rise to crystallographically faceted pits. The surface mobility of oxygen and silicon atoms present during growth is driven towards preferential absorption and accumulation at pits containing facets along particular planes such as (10\( \overline{1} \)0) and (10\( \overline{1} \)1). As a result, most probably, the density of active dopants decreases.

Some incorporation of Si and O atoms as substitutional defects in the crystal lattice must occur. Their fraction, though, is seemingly not enough as to give rise to any signal in the respective EPR spectra taken from any of the layers with pit-populated morphology (Fig. 4, the EPR spectrum corresponding to the layer T1 in the labels of Fig. 2). Besides the layers with typical thickness of \( \sim 360 \text{nm} \) included in this study, the investigation has also been concerned with layers of substantial thickness, \( \sim 2 \mu\text{m} \), as to increase the volume of the probed material and improve the collected signal/noise ratio in the EPR spectra. Furthermore, such thick layers contained oxygen at the level of \([\text{O}] \sim 4 \times 10^{17} \text{cm}^{-3} \) being two orders of magnitude less than the incorporated Si to minimize the effect of any potential O-related compensation.

Notably, EPR spectra in darkness at 5 K are recorded from the Al0.77Ga0.23N:Si layers with thickness of \( \sim 360 \text{nm} \) characterized by a smooth and pit-free surface morphology resulting from applying low grow rate and moderate doping of \([\text{Si}] \sim (2-3) \times 10^{18} \text{cm}^{-3} \) (Fig. 4, the EPR spectrum corresponding to the layer L1 in the labels of Fig. 2). As already pointed out, these layers yield resistivity of less than 0.05 \( \Omega \text{ cm} \) for electron mobility of 80 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) at carrier concentration of low \( 10^{18} \text{cm}^{-3} \). Illumination with white light induces relative changes in the line shape and the g-value but not the total intensity of the EPR spectrum. The relative changes of the EPR spectrum are attributed mainly to the presence of two donors, Si and O, and their overlapping contribution to the total signal. In darkness, and at low temperature, the population of carriers is higher on the apparently deeper O level. This gives rise to a relatively broader line with a g-value of \( g = 1.9848 \pm 0.0001 \) due to a larger contribution of O to the total EPR signal. A broad signal may be expected from the substitutional O\( _2 \) donor following the discussion in Ref. 11, and based on arguments about the hyperfine interactions between the unpaired electron spin and the nuclear spins of nearest neighbors in the Al(Ga) sub-lattice. Under illumination, carriers redistribute with increasing the population on the Si level giving rise to a narrower line width expected for the Si shallow donor. The insensitivity of the EPR intensity on illumination indicates that carrier compensation by traps in the upper part of the band gap, including traps associated with oxygen, is negligible. This is to be particularly noted as the oxygen concentration in these Al0.77Ga0.23N:Si layers increases by one order of magnitude from \([\text{O}] \sim 3 \times 10^{17} \text{cm}^{-3} \) in the layer L2* to \([\text{O}] \sim 2 \times 10^{18} \text{cm}^{-3} \) in the layer L1 [Fig. 2]. The findings of the EPR study suggest that silicon and oxygen behave as shallow donors in the high-Al-content layers of Al0.77Ga0.23N alloy composition.
The growth rate is inversely proportional to the input metal-organic gas flow, and a low growth rate benefits the implementation of a smooth surface topography for high enough process temperature and low enough flow rate, a low growth rate benefits the implementation of a smooth surface topography for high enough process temperature and low enough growth rate is the development of a smooth surface topography.

FIG. 5. Ratio of carrier concentration (n) to the total concentration of incorporated Si and O atoms, n/(Si + O), vs. the increase of atomic concentration of major impurities O and C as measured by SIMS.

Acknowledging that both Si and O may potentially contribute carriers for the n-type conductivity of the Al0.77Ga0.23N:Si layers studied here, we further consider the ratio of carrier concentration (n) to the total concentration of incorporated Si and O atoms. A rather high ratio of n/(Si + O) ~ 0.80 is generally determined, particularly for [Si] dominating [O] within a factor of about 10 (Fig. 5, the layer L2*). In the Al0.77Ga0.23N:Si layers with intentional doping level of Si ~ (2−3) x 10^17 cm^-3 studied here, the concentration of major impurities O and C changes independently on the Si concentration but in apparent correlation with each other [Fig. 5]. As both, the O and C atomic concentration increases to become comparable to that of the Si atomic concentration, the ratio of n/(Si + O) drops to 0.55. This layer still retains the transport properties of its partner layers L2* and L2 in terms of carrier concentration of n ~ 2 x 10^18 cm^-3. However, a certain level of carrier compensation is apparent as the total concentration of the incorporated Si and O atoms in the layer L1 is ([Si] + [O]) ~ 4 x 10^18 cm^-3. The carrier compensation plausibly involves C as well as O impurities, especially considering their interrelated incorporation into the studied Al0.77Ga0.23N:Si layers. Obviously, the implemented growth conditions have resulted in a certain balance of the incorporated intrinsic and substitutional point defects. The potential of substitutional O to contribute free carriers must be precluded by its involvement in the formation of defect complexes likely located in the lower half of the band gap.

In conclusion, the dopant and impurity incorporation kinetics, as established by applying a high process temperature together with a low growth rate, is implicit in the control of n-type high-Al-content Al0.77Ga0.23N:Si layers. The criterion for high enough process temperature and low enough growth rate is the development of a smooth surface topography preventing faceting, which can cause pits formation indicated to be detrimental for the transport properties of the layers. Following the kinetics of the Si incorporation, which is inversely proportional to the input metal-organic gas-flow rate, a low growth rate benefits the implementation of a reduced SiH4 flow to retain a pit-free morphology yet achieving the relevant Si incorporation for efficient carrier concentration. The EPR study was only possible on Al0.77Ga0.23N:Si layers of pit-free morphology. The EPR study suggests Si and O to behave as shallow donors. Carrier compensation by traps in the upper part of the band gap, including traps associated with oxygen, is negligible, even in the layers with comparable concentration of Si and O in the range of 10^18 cm^-3. Certain mechanism of carrier compensation by traps in the lower part of the band gap, however, is given rise at these moderate O concentrations (indicated by the drop in the ratio n/(Si + O)). It appears relevant to be put in the context of the observed interrelated incorporation of the other major impurity established in the layers, namely, carbon.

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