Improving the conductivity limits in Si doped Al rich AlGaN

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***Abstract*— We report point defect control of two primary compensating defects in AlGaN: C_N and V_{III}+nSi_{Al}, based on their dependence on chemical potentials. Reasonable control over the knee behavior of the conductivity and the low doping limit in $Al_{0.65}Ga_{0.35}N$ thin films grown on sapphire is achieved.**

Keywords—AlGaN, knee behavior, point defect control, conductivity

I. INTRODUCTION

AlGaN with a tunable wide direct bandgap from 3.4 eV (GaN) to 6.03 eV (AlN), high internal quantum efficiencies and a high critical breakdown field ranging from 3.75 MVcm^{-1}(GaN) to 15 MVcm^{-1}(AlN) has generated tremendous interest in the fields of UV optoelectronics and high-power electronics. However, significant challenges in point defect control in AlGaN epitaxy has precluded commercialization of many AlGaN based devices. Si is typically employed as n-type dopant in AlGaN and exhibits a low activation energy (<50 meV) in $Al_xGa_{1-x}N$ with x<0.8.[1] However, Si doped AlGaN exhibits a "knee behavior" of resistivity as a function of Si incorporation, with resistivity increasing with increase in Si incorporation beyond a minimum value for a specific Si concentration.[2] This produces a high doping limit for Si in AlGaN that lowers the maximum achievable carrier concentrations that are necessary for AlGaN based opto-electronics. Further a low doping limit (a minimum achievable carrier concentration with a corresponding maximum mobility) exists in AlGaN which precludes implementation of AlGaN power electronics that require low doped drift regions. Various efforts in point defect control in III-Nitrides primarily by varying growth conditions such as precursor gas flows, growth temperature, diluent gas flows, pressure etc. have been attempted to improve conductivity.[3]–[7] Recently, we demonstrated a systematic chemical potential control (CPC) based point defect control by relating the growth environment variables with the defect formation energy through chemical potentials allowing for growth environment optimization for minimal defect incorporation in GaN.[8] Accordingly, we employ and extend CPC based point defect reduction to AlGaN and control the identified point defects responsible for doping limits.

II. CHEMICAL POTENTIAL CONTROL

The tendency to incorporate a specified defect during growth processes may be represented by the formation energy of the defect. For a defect X with charge state q, in a material at equilibrium, it is defined as:

$$E^f\left(X^q\right) = E_{ref}\left(X^q\right) - \sum_j n_j \mu_j + q\left[E_F + E_V\right], \qquad (1)$$

where E_{ref} is the free energy of the crystal with a single defect referenced to the free energy of the ideal crystal, n_j is the number of atoms of jth type exchanged with the reservoir to form the defect and μ_j is the associated chemical potential. E_F is the Fermi energy referenced with respect to the valence band maximum. The chemical potentials of the metals are given by[8]

$$\mu_{Ga} = kT \log\left(\frac{P_{eq}^{Ga}}{P_V^{Ga}}\right) \qquad (2)$$

$$\text{and } \mu_{Al} = kT\log\left(\frac{P_{eq}^{Al}}{P_V^{Al}}\right), \qquad (3)$$

where P_{eq} is the equilibrium partial pressure of Al(Ga) atoms at the surface during growth and P_V is the vapor pressure of corresponding metal at equilibrium at the growth temperature. The equilibrium partial pressures of Al(Ga) atoms are calculated using the thermodynamic growth model for MOCVD AlGaN described in [9] and hence the chemical potential at a particular growth state may be determined. More importantly, the change in chemical potentials between two growth states i.e. change in formation energy of the defect between two growth states may be determined. Hence employing the known growth variables, the growth environment producing the highest formation energy for a specified defect within practical constraints may be determined. Here, we define a standard or reference growth state with corresponding reference chemical potentials. The difference in the chemical potential of Al($\Delta\mu_{Al}$) or Ga($\Delta\mu_{Ga}$) atoms between a specified growth state and the predefined reference growth state is obtained by

$$\Delta\mu_{Ga} = kT\log\left(\frac{P_{eq}^{Ga}}{\left[P_{eq}^{Ga}\right]_{ref}}\right) \qquad (4)$$

$$\text{and } \Delta\mu_{Al} = kT\log\left(\frac{P_{eq}^{Al}}{\left[P_{eq}^{Al}\right]_{ref}}\right), \qquad (5)$$

where the subscript 'ref' refers to the equilibrium partial pressure in the reference growth state. In order to determine the chemical potential of nitrogen, the following equilibrium is assumed in the alloy $Al_xGa_{1-x}N$

$$xAl + (1-x)Ga + N \leftrightarrow Al_xGa_{1-x}N, \qquad (6)$$

and hence

$$x\mu_{Al} + (1-x)\mu_{Ga} + \mu_N = \mu_{Al_xGa_{1-x}N}. \qquad (7)$$

From (7), the difference in the chemical potential of nitrogen between the specified growth state and the reference growth state can be determined by

$$\Delta\mu_N = -\left[x\Delta\mu_{Al} + (1-x)\Delta\mu_{Ga}\right]. \qquad (8)$$

Hence employing the thermodynamic model for AlGaN growth along with (4), (5) and (8), the change in the nature of the growth environment i.e. chemical potentials of Al,Ga and N may be determined with respect to a reference growth state.

III. DEFECTS OF INTEREST

The required growth environment to reduce the compensating defects may be determined only after identifying the defects responsible for limiting the conductivity by compensation. Accordingly, vacancy-silicon complexes were determined as the defects responsible for the knee behavior i.e. high doping limit in MOCVD AlGaN.[10] The low doping limit has several sources including dislocations, C_N and vacancy-oxygen complexes.[2] In this work, we study the control of C_N.

A. Vacancy-silicon complex

The formulation of energy of formation and chemical potentials is described in [8] and is extended to vacancy silicon complex here. The formation energy of the V_{III}+nSi_{Al} complex may be written as[10]

$$E^f\left(\left(V_{III} + nSi\right)^{-t}\right) = E_{ref}\left(\left(V_{III} + nSi\right)^{-t}\right) + \mu_{III} - n\mu_{Si} - t\left[E_F + E_V\right] \qquad (9)$$

where the charge of the complex, -t, is dependent on number of silicon atoms in the complex n and t=3-n. It is clear from (9), the change in the formation energy of V_{III}+nSi_{Al} complex is dependent on changes in chemical potentials of metal μ_{III} and silicon μ_{Si}, and hence is written as

$$\Delta E^f\left(\left(V_{III} + nSi\right)^{-t}\right) = \Delta\mu_{III} - n\Delta\mu_{Si}. \qquad (10)$$

where $\Delta\mu_{III} = \left[x\Delta\mu_{Al} + (1-x)\Delta\mu_{Ga}\right] = -\Delta\mu_N$ from (8), by following the procedure described in [8]. Hence reduction of self-compensation due to vacancy silicon complex requires a nitrogen poor/metal rich growth environment.

B. Carbon at nitrogen lattice site

Reduction of C_N compensation by CPC is described in [8] and requires a nitrogen rich growth environment and the change in the formation energy of C due to changes in chemical potentials may then be written as

$$\Delta E^f\left(C_N\right) = \Delta\mu_N - \Delta\mu_C. \qquad (11)$$

Assuming boundary phase of C in AlGaN to be identical to that in GaN, i.e. CN, the change in the chemical potential of C, $\Delta\mu_C$ (as demonstrated in [8]) is approximately given by

$$\Delta\mu_C = -\Delta\mu_N, \qquad (12)$$

and hence the change in the energy of formation is given by

$$\Delta E^f\left(C_N\right) = 2\Delta\mu_N. \qquad (13)$$

It is obvious that C reduces with increase in chemical potential of nitrogen. Hence reduction of C_N compensation requires a nitrogen rich growth environment.

IV. EXPERIMENTAL

AlGaN layers were grown on AlN templates on top of c-plane α-Al_2O_3 (sapphire) in a vertical, rf-heated low-pressure MOCVD reactor equipped with an open showerhead. Sapphire substrate treatment before growth included annealing in H_2 ambient at 1100°C for 7 minutes and nitridation at 950°C for 4 minutes. A 20 nm low temperature AlN nucleation layer was deposited at 650°C and then annealed at 1050°C for 15 minutes to obtain Al-polarity. After the annealing process, the 300 nm thick AlN layer was grown to serve as a template for doped AlGaN growth. The dislocation density (DD) on AlN template on sapphire was ~10^{10} cm^{-2}.

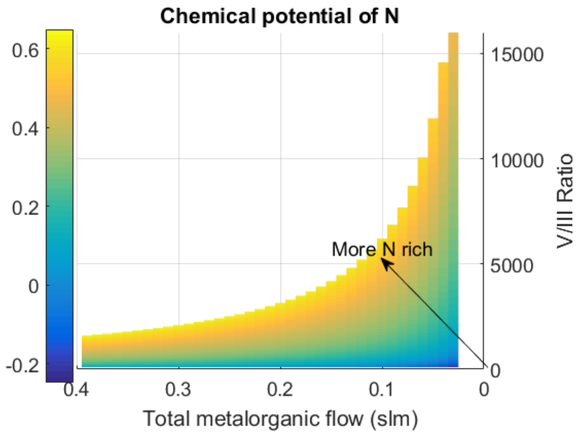

Figure 1: The change in the chemical potential of N as a function of metalorganic flow and V/III ratio with the reference defined at standard growth conditions (growth temperature of 1100 °C, H_2 diluent, gas flow rate of 10 slm, an NH_3 flow rate of 0.3 slm, a TEG flow rate of 11.4 µmol/min and a TMA flow rate of 22.2 µmol/min).

The reactor total pressure was kept constant at 20 Torr throughout the growth. Trimethylaluminum (TMA), triethylgallium (TEG), and NH_3 were used as Al, Ga, and N precursors, respectively. SiH_4 was used as the Si dopant source. Subsequently, AlGaN layers were grown in H_2 diluent gas flowing of 10 slm. Al mole fraction in strained AlGaN layer on AlN/sapphire template was determined by the relative measurement between AlN and AlGaN peaks. The details of the composition measurement technique is described in [11]. Hall measurements were performed using Van der Pauw geometry with V/Al/Ni/Au metal stacks as ohmic contacts.[12] AlGaN films were grown with varying NH_3 flow from 0.3 slm to 3 slm and growth temperature was maintained At 1100 ºC. The AlGaN thin films were then characterized by hall measurements employing Ecopia HMS3000.

V. RESULTS AND DISCUSSION

Since the dependence of the formation energy of the defects on the chemical potentials of Al,Ga and N are known, we can develop a chemical potential map as a function of growth parameters such as ammonia and metal organic flows and determine the growth environment necessary to reduce specified defects. Accordingly, by applying the developed chemical potential and thermodynamic growth models, the change in the chemical potential of N is plotted as a function of metalorganic and V/III ratio in Fig. 1. It is clear that the growth environment becomes more N rich with increase in V/III ratio at any given metalorganic flow and may be quantified. Finally, the dependence of the formation energy of the defects may then be quantified by (10) and (13) for V_{III}+nSi and C_N respectively.

Hence, the chemical potential control i.e. tuning the growth environment towards N rich or metal rich conditions was achieved by growing AlGaN films with varying NH_3 flow at a constant TEG flow rate of 11.4 µmol/min and a TMA flow rate of 22.2 µmol/min. The AlGaN thin films were characterized by photoluminescence where, defect luminescence corresponding to C_N and V_{III}+nSi was employed to quantify the change in defect formation/incorporation. As expected, the C incorporation decreases with increase in ammonia partial pressure and vacancy-silicon complex increases with increase in ammonia partial pressure. This is clearly seen by the transition of the defect luminescence from C_N to V_{III}-nSi with increase in ammonia flow from 0.3 slm to 1 slm as shown in Fig. 2. The silicon concentration was approximately ~$1\text{x}10^{19}$ cm^{-3} and corresponds to a doping concentration slightly below the knee at 0.3 slm NH_3 flow. Accordingly, Fig. 3 summarizes the dependence of conductivity of Si-doped AlGaN on silicon chemical potential (i.e. silane flow) and chemical potential of III-metal/N. In agreement with photoluminescence results, the C incorporation (the low doping limit) decreases with increase in ammonia partial pressure resulting in an increase in conductivity (at low silane flows shown by solid line with upward arrow) from 0.3 slm to 3 slm. Further the transition from C_N peak to the vacancy peak in the photoluminescence measurements indicates that the onset of self-compensation (due to vacancies) is shifted to lower silicon concentrations with increase in ammonia partial pressure as predicted by the model due to lowered formation energies. This is seen in the electrical results in Fig. 3, where the vacancy complex related compensation (the high doping limit or onset of knee-behavior) increases with increase in ammonia partial pressure resulting in the onset of self-compensation at lower silane flows at higher ammonia partial pressures. This results in higher peak conductivity at lower ammonia flows (dashed line with arrow) and corresponds to higher silane flows as shown in Fig. 3.

VI. CONCLUSION

In conclusion, we have demonstrated point defect control of the two primary compensating defects in Al rich AlGaN: C_N and V_{III}+nSi_{Al}, by chemical potential control and have shown reasonable control over the knee behavior, peak conductivity and low doping limits in AlGaN.

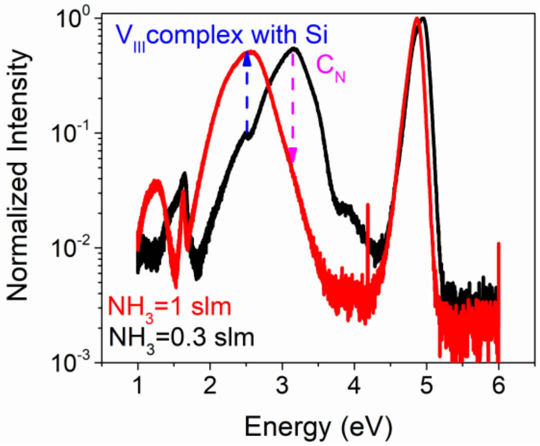

Figure 2: The normalized photoluminescence spectra for $Al_{0.65}Ga_{0.35}N$ shown as a function of NH_3 flow with a silicon concentration ~10^{19} cm^{-3}.

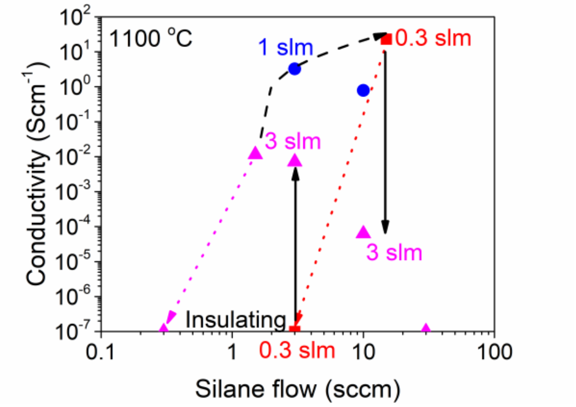

Figure 3: Conductivity as a function of silicon incorporation (silane flow) at different ammonia flows at a constant growth temperature being 1100 °C. The pink triangles, blue circles and red squares represent growths at ammonia flows of 3 slm, 1 slm and 0.3 slm respectively. The dotted lines represent a decrease in conductivity to an insulating behavior.

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