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Unintentionally doped *n*-type $Al_{0.67}Ga_{0.33}N$ epilayers

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Unintentionally doped $Al_{0.67}Ga_{0.33}N$ epilayers were grown on AlN/sapphire templates by metalorganic chemical vapor deposition. Optimized undoped $Al_{0.67}Ga_{0.33}N$ epilayers exhibited an *n*-type conductivity as confirmed by Hall-effect measurement with a room-temperature resistivity of about 85 Ω cm. Variable temperature Hall-effect measurement revealed the existence of a shallow donor level with activation energy of about 90 meV. The photoluminescence (PL) spectra exhibited an emission peak at 4.13 eV (4.06 eV) related to an impurity transition at 10 K (300 K). Temperature dependent PL measurement also confirmed the existence of a shallow donor with comparable activation energy as that obtained by Hall-effect measurement. Isolated oxygen impurities are believed to be a strong candidate of the donor that remains as a shallow state in $Al_xGa_{1-x}N$ up to $x \sim 0.7$. Compensating defects and the nature of the O donor in $Al_{0.67}Ga_{0.33}N$ epilayers are also discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1954875]

AlGaN alloys are promising for applications in chip-scale emitters and detectors operating at wavelengths down to 200 nm. Tremendous progress in research and development has been made in understanding the fundamental properties of these materials as well as their practical applications. However, our understanding of fundamental properties of Al-rich AlGaN alloys is much less than that of GaN. The cause of background concentration of free electrons in undoped GaN grown by metalorganic chemical vapor deposition (MOCVD) had been an issue of debate in the last decade. For many years, it was believed that the intrinsic defects like nitrogen vacancies (V_N) are the cause of the background *n*-type conductivity in undoped GaN. Nonetheless, the first principle calculations excluded V_N as the source of *n*-type conductivity as its formation energy is large.[1] Unintentionally doped oxygen, whose energy level is about 30 meV, is believed to be the donor source in undoped GaN.[1–3] However, the conductivity of undoped AlGaN alloys decreases with increasing Al content and high Al-content $Al_xGa_{1-x}N$ alloys ($x > 0.4$) often behave as insulators.[4] It was proposed that the decrease in conductivity with increasing Al content in undoped $Al_xGa_{1-x}N$ is due to the transition of oxygen from shallow donor into DX center.[5] Conductivity also decreases with increasing Al content in Si-doped AlGaN, mainly due to the deepening of Si donor level, compensation with acceptor like defects, and increase in dislocation density.[6,7]

Recently, there have been several reports on the achievement of highly conductive *n*-type Si-doped Al-rich AlGaN alloys.[7–11] The problem for achieving highly conductive AlGaN materials was identified as mainly due to the incorporation of compensating acceptor-like defects such as aluminum vacancies (V_{Al}) or $V_{Al}-O_N$ complexes. We have developed a growth technique to suppress aluminum vacancies and/or complexes in Al-rich AlGaN epilayers and achieved a resistivity of 0.0075 Ω cm with a free electron concentration of 3.3×10^{19} cm^{-3} and mobility of 25 cm^2/V s for Si-doped $Al_{0.7}Ga_{0.3}N$ at room temperature.[11,12] Such an achievement inspired us to explore the undoped Al-rich AlGaN alloys. Many basic questions such as the conductivity control, role of oxygen impurities, cause of compensation, etc., can be addressed through the investigation of undoped materials.

In this letter, we report on the growth, electrical, and optical properties of unintentionally doped $Al_{0.67}Ga_{0.33}N$ epilayer grown by MOCVD using similar techniques as in the previous study.[11,12] By further suppressing compensating defects, we have obtained *n*-type conductivity in undoped $Al_xGa_{1-x}N$ epilayers for $x \sim 0.67$ at room temperature. Optimized $Al_{0.67}Ga_{0.33}N$ epilayers exhibit *n*-type resistivity about of 85 Ω cm at room temperature as confirmed by Hall-effect measurement. Temperature dependent Hall-effect and photoluminescence (PL) measurements show that there is a shallow donor with an activation energy of about 90 meV. Possible candidates of the donor and compensating defects in AlGaN alloys are also discussed.

Unintentionally doped $Al_{0.67}Ga_{0.33}N$ epilayers of thickness ~1 μm were grown on AlN/sapphire template by MOCVD. An AlN epilayer of thickness ~0.5 μm was first deposited on sapphire substrate followed by the growth of an AlGaN epilayer. The insertion of a high quality AlN epilayer is essential in suppressing the compensating defects in the subsequent AlGaN layer. The metalorganic sources used were trimethylgallium and trimethylaluminum for gallium and aluminum, respectively. Blue ammonia was used as nitrogen source. X-ray diffraction was used to determine the aluminum content and crystalline quality. The AlGaN epilayers have a typical full width at half maximum of rocking curve of the (0002) peak of about 500 arcsec. Atomic force microscope was used to characterize the surface morphology. No crack was found on the surfaces. Transport properties were studied by variable temperature Hall-effect measurements. Deep UV PL spectroscopy system was employed to study the optical properties and to probe the impurities. The PL system consists of a frequency quadrupled 100 fs Ti: sapphire laser with an average power of about 3 mW at 196 nm and repetition rate of 76 MHz. The impurity concentrations in the samples were determined by secondary ion mass spec-

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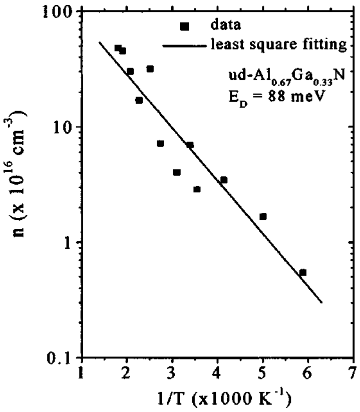

FIG. 1. The temperature dependence of the free electron concentration (n) in an unintentionally doped $Al_{0.67}Ga_{0.33}N$ epilayer. The solid line is a linear fit of the experimental data with the relation $n(T) \propto \exp(-E_D/kT)$ with the fitted activation energy E_D of 88 meV.

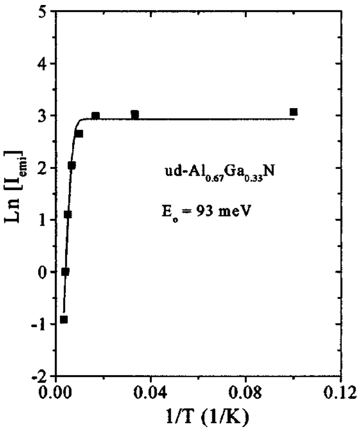

FIG. 3. The Arrhenius plot of the integrated PL intensity of the 14.13 eV emission line. The solid line is the least squares fit of the experimental data with Eq. (1) with a fitted activation energy E_o of 93 meV.

troscopy (SIMS)measurement (performed at Charles Evans & Associates).

Figure 1 shows the semilog plot of free electron concentration (n) vs $1/T$ of an undoped $Al_{0.67}Ga_{0.33}N$ epilayer. The free electron concentration increases exponentially with increasing temperature. At room temperature, n-type resistivity value measured is about 85 Ω cm, however, with a low electron mobility ($\sim 2\ cm^2/V\ s$). This could be due to the large alloy scattering and increased effective mass of electrons for such a high Al content AlGaN alloy. The solid line is the least squares fitting with the relation, $n(T) \propto \exp(-E_D/kT)$, where $n(T)$ is the free electron concentration at temperature T and E_D is the donor activation energy. The fitted E_D is found to be 88 meV. This shows that there is an unintentional shallow donor in $Al_{0.67}Ga_{0.33}N$ epilayers contributing to n-type conductivity.

PL spectra of undoped $Al_{0.67}Ga_{0.33}N$ epilayers in the temperature range from 10 to 300 K are shown in Fig. 2. There is a strong emission at 4.13 eV at 10 K, which shifted to 4.06 eV at room temperature. There is also a broadening of PL spectrum with increasing temperature. Figure 3 shows the Arrhenius plot of the integrated PL intensity of the emission peak at 4.13 eV (10 K). The solid line is the least squares fitting of data with the following equation:[13]

$$I(T) = \frac{I_o}{1 + ce^{-E_o/kT}}, \tag{1}$$

where $I(T)$, and $I(0)$ are the integrated PL intensity at temperature T and 0 K, and E_o is the PL emission intensity activation energy. The fitted value of the activation energy (E_o) is 93 meV. This value is close to the activation energy determined from the temperature dependent Hall-effect measurement. This indicates that the PL emission peak at 4.13 eV involves the transition of electrons bound to shallow donors with a binding energy between 88 and 93 meV. An acceptor with such a shallow binding energy is not expected and can thus be excluded. We believe the emission peak at 4.13 eV is due to the transition between a shallow donor to a deep acceptor, which is also consistent with the energy levels expected from $Al_{0.67}Ga_{0.33}N$ alloys. The formation energies of cation vacancies (V_{III}) such as V_{Al} and $V_{Al}-O_N$ complexes are small for n-type AlGaN. They can be a triple, double, or single charged state.[6,14] We believe that the acceptors-like defects are significantly suppressed in this sample. It is remarkable that the compensation can be suppressed to such a low level that undoped Al-rich $Al_xGa_{1-x}N$ $(x=0.67)$ can be grown n type. We believe that the use of high quality AlN epilayer as a template plays a crucial role in suppressing V_{III} and its related complexes and that further optimizing growth conditions and improvement of material quality will further suppress compensating defects and improve the conductivity in undoped Al-rich AlGaN epilayers.

The results from Hall-effect and PL measurements confirm that there is a shallow donor in undoped $Al_{0.67}Ga_{0.33}N$ epilayer. This naturally leads to the question: "what would be the possible origin of the donors?" Similar to GaN, the formation energy of V_N in $Al_xGa_{1-x}N$ for Fermi level near the conduction band is large and the binding energy of V_N for $x \sim 0.7$ is about 0.2 eV.[15] Hence V_N is unlikely to be the shallow donor observed here, similar to GaN. Oxygen and carbon are commonly present in the MOCVD grown materials as unintentionally doped impurities. Oxygen is believed to be a shallow donor in undoped GaN whose activation energy is about 30 meV.[3] Figure 4 shows the SIMS profiles of oxygen and carbon impurities in an $Al_{0.67}Ga_{0.33}N$ epilayer. Concentration of oxygen [O] is about $8 \times 10^{18}\ cm^{-3}$ and that of carbon is in the middle of $10^{17}\ cm^{-3}$. Carbon is also believed to be an acceptor.[16] Similar to undoped GaN, we thus

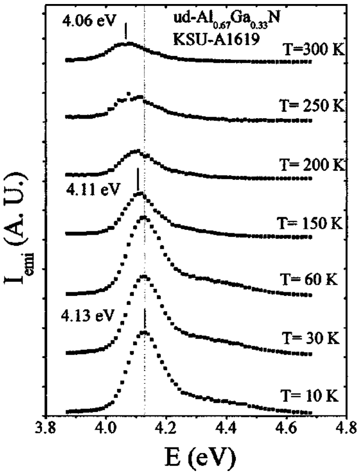

FIG. 2. PL spectra of an unintentionally doped $Al_{0.67}Ga_{0.33}N$ epilayer measured between 10 and 300 K.

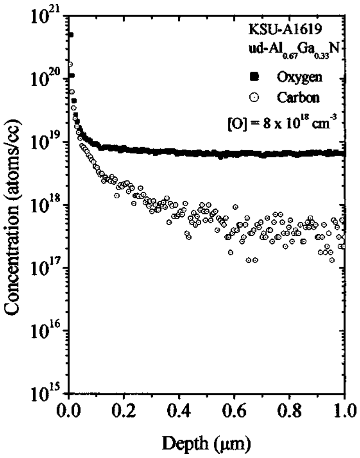

FIG. 4. Secondary ion mass spectrometry (SIMS) profiles of oxygen and carbon impurities in an undoped $Al_{0.67}Ga_{0.33}N$ epilayer.

believe that oxygen could be a strong candidate of the donor impurities in undoped $Al_xGa_{1-x}N$ alloys for x up to 0.7.

The nature of oxygen is predicted to be different in GaN and AlN, although most of the other defects are similar. Theoretical calculations indicated that oxygen is a shallow donor in GaN, however it is a DX center in AlN.[17] However, DX-like metastability behavior was not observed in these undoped $Al_{0.67}Ga_{0.33}N$ epilayers here. Pophristic, Guo, and Peres[9] also observed experimentally that the resistivity of Si-doped $Al_xGa_{1-x}N$ films decreases with increasing oxygen concentration for $x \sim 0.6$, giving evidence that oxygen may not undergo DX transition up to $x \sim 0.6$. Thus, isolated oxygen impurities could be a strong candidate as a donor that remains as a shallow state in $Al_xGa_{1-x}N$ alloys for x up to 0.7. Though it is more difficult to grow Al-rich AlGaN alloys, the intrinsic electric properties of low defect content Al-rich AlGaN alloys are similar to GaN—both of which may be n type for unintentionally doped materials. Similarity between GaN and Al-rich AlGaN alloys implies that the knowledge we accumulated in the last decade for GaN may be extended for the understanding of Al-rich AlGaN alloys.

In summary, we have grown n-type undoped $Al_{0.67}Ga_{0.33}N$ epilayer by MOCVD with a resistivity of about 85 Ω cm at room temperature. The findings of our work revealed that (i) compensating defects in Al-rich AlGaN can be suppressed to a level that unintentionally doped Al-rich AlGaN can be grown n type, (ii) there exists a shallow donor of about 90 meV below the conduction band, and (iii) isolated oxygen impurities are a strong candidate of the donor that remains as a shallow state in $Al_xGa_{1-x}N$ up to $x \sim 0.7$. We believe that additional improvements in material quality and suppression of deep acceptors in AlGaN alloys would further enhance the material conductivity.

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