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Effect of ammonia flow rate on impurity incorporation and material properties of Si-doped GaN epitaxial films grown by reactive molecular beam epitaxy

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I. INTRODUCTION

The great potential of III-nitride materials for optoelectronic and electronic devices has been realized by the recent achievement of high luminescence light-emitting diodes, l blue laser diodes working at room temperature, 2 and modulation-doped field effect transistors. 3 High quality n and p type, as well as undoped, GaN films play important roles in the performance of these devices.

The Hall mobility of Si-doped GaN films grown by the metalorganic chemical vapor deposition (MOCVD) technique has been improved by employing either low-temperature AlN or GaN buffer layers. By using an AlN buffer layer, the room-temperature Hall mobility was increased by approximately one order of magnitude from 10–30 to 350–400 cm2/V s. 4 The highest room-temperature Hall mobility ever reported was 900 cm2/V s for a GaN film grown on a thin GaN buffer layer by the MOCVD technique. 5 Although Hall mobilities of 255 and 160 cm2/V s with doping levels of $5 \times 10^{17}$ and $3 \times 10^{18}$ cm$^{-3}$, respectively, have been reported for GaN films grown by reactive molecular beam epitaxy (RMBE), 6 the effect of experimental parameters such as buffer layer, ammonia flow rate (V/III ratio when Ga flux is kept constant), film thickness and growth temperature on the material characteristics of Si-doped n-type GaN films grown by the RMBE technique has not been reported yet.

Since ammonia is commonly used as a precursor for the nitrogen species in the MOCVD, hydride vapor phase epitaxy (HVPE) and RMBE growth techniques, it is important to determine the effect of ammonia flow rate on the growth and material properties of GaN films. The effect of ammonia flow rate on the impurity incorporation of undoped and Mg-doped GaN films grown by RMBE has been reported recently. 7 In this study, the effect of ammonia flow rate on the impurity incorporation and material properties of Si-doped GaN films grown by RMBE has been investigated.

II. EXPERIMENT

A Riber 1000 MBE system equipped with turbomolecular pump was used to grow GaN films by the RMBE process. Details of the growth process are described in previous reports. 5 Three Si-doped GaN films with different Si concentrations were grown for the impurity study. The ammonia...
flow rate was changed in several steps throughout each growth. The depth profile of impurities along the growth direction was obtained by secondary ion mass spectroscopy (SIMS) performed at Charles Evans & Associates using a CAMECA IMS-4f double focusing ion microanalyzer configured for cesium primary ion bombardment. The H, O, and Si signals were analyzed under the negative secondary ion acquisition configuration, and the depth profiles were acquired by monitoring the M⁻ ions, where M represents the element of interest. The quantification of elemental concentrations for these impurities was performed using relative sensitivity factors (RSFs) derived from the analyses of standard GaN samples with known doses of impurity implants.

Two other series of Si-doped GaN films were grown with different ammonia flow rates ranging from 5 to 73 sccm using an AIN buffer layer grown on c-plane sapphire as the substrate. For one series (set I) of Si-doped films, highly resistive undoped GaN (~1.5 μm thick) was grown beneath the Si-doped top layer (~1.5 μm thick). These highly resistive layers were grown at the substrate temperature of 750 °C with low ammonia flow rates (5–8 sccm), and the Si-doped layers were grown at the same temperature with different ammonia flow rates. The second series (set II) of Si-doped films was grown at 800 °C without the highly resistive GaN buffer layer. The growth rate employed was approximately 1.2±0.1/h. Electrical characteristics of the films were measured by the van der Pauw method. The photoluminescence (PL) measurements were performed using the 325 nm excitation line of a He–Cd laser. A Ti/Al/Ti/Au multilayer, alloyed at 900 °C for 30 s by rapid thermal annealing (RTA) under nitrogen atmosphere, was utilized as the electrical contact to the GaN films.

For deep level transient spectroscopy (DLTS) measurements, three Schottky barrier diode (SBDs) structures were grown with 2-μm-thick n⁺ layers for ohmic contact on top of an AIN buffer layer followed by 0.5-μm-thick n layer for the Schottky layer. The thick n⁺ contact layers were grown with 60 sccm ammonia flow rate and the top Schottky layers were grown with 20, 60, and 73 sccm ammonia flow rates, respectively. Mesa structures with 250 μm diameter were produced by reactive ion etching. Each mesa was surrounded by large area Ti/Al/Ti/Au ohmic contacts, vacuum deposited and annealed by rapid thermal annealing at 950 °C for 30 s, with 50 μm spacing between contacts and mesas. Then, 200 μm diameter Au/Ni dots were deposited by vacuum evaporation on the surfaces of the mesas as Schottky contacts. The mesa surface was cleaned by aqua regia solution followed by DI water cleaning to prevent parasitic capacitance resulting from residual contaminants on the surface.

A Bio-Rad DL 4600 DLTS system with a 100 mV test signal at 1 MHz was used to carry out capacitance–voltage (C–V) and DLTS measurements. The C–V data, used to establish carrier profiles, were taken at different temperatures to determine whether the carrier concentration was changing with temperature or if the carriers froze out at low temperature. Provided that the carrier concentration is much larger than the trap concentrations at all temperatures, the DLTS system can automatically display the trap concentration versus temperature directly, based on Lang’s approximate equation, \( N_T = 2N_D \Delta C/C \), where \( N_T \) is the trap concentration for a DLTS peak, \( N_D \) is the uniform ionized donor concentration; \( \Delta C \), the amplitude of the DLTS peak; and \( C \), the diode quiescent capacitance under reverse bias, respectively.3 During the DLTS measurements, a reverse bias of a few volts (depending on the sample tested) was applied to the SBD and periodically pulsed to 0 V, with a pulse width of 1 ms, to fill the traps. To determine the apparent parameters of the electron traps, i.e., the activation energy \( E_T \) and the capture cross section \( \sigma_T \), the DLTS spectra were taken at different rate windows from 20 to 1000 s⁻¹.

Transmission electron microscopy (TEM) was used to characterize the film microstructure. Samples were prepared for observation in the cross-sectional geometry using mechanical slicing, polishing and argon-ion milling to perforation. Observations were made with a JEM-4000 EX transmission electron microscope at the operation voltage of 400 kV. Interpretable resolution limit was about 0.16 nm. High-resolution images were recorded at close to the optimum objective lens defocus of ~48 nm without an objective aperture. Lower magnification images were recorded with a small objective aperture to enhance contrast from growth defects.

III. RESULTS AND DISCUSSION

A. Impurity incorporation

The effect of ammonia flow rate on the incorporation of Mg, O, Si, and H into undoped and Mg-doped GaN films was discussed previously.7 Three Si-doped GaN films with different Si concentration were grown to investigate the incorporation of H, O, and Si into Si-doped films. It was reported that the hydrogen concentration remained well below the Si concentration and that the Si concentration was largely unaffected by the presence of hydrogen.9 Figure 1 shows the depth profile of H, O, and Si measured by SIMS for these three films. The secondary ion intensity for matrix element was also shown to distinguish the interface between the GaN film and the substrate. Unlike hydrogen profiles for Mg-doped GaN films, the hydrogen concentration here does not change with the ammonia flow rate and it does not seem to affect the incorporation of Si into the GaN films grown by the RMBE process. However, the hydrogen concentration is not far below the Si concentration, and it remains relatively constant at around 10¹⁸ cm⁻³ for all three samples shown in Fig. 1.

The extraordinarily high concentration of oxygen atoms for the initial 1-μm-thick film seen in Figs. 1(a) and 1(b) reflects either inferior crystal quality or out-diffusion from the substrate. Discussion in this section will exclude this highly contaminated region. For the film with Si concentration about 3×10¹⁷ cm⁻³ shown in Fig. 1(a), the oxygen level is almost constant. However, for the other two films shown in Figs. 1(b) and 1(c), the oxygen concentration decreases when the ammonia flow rate is increased. A possible explanation for this trend could be a competition between nitrogen and oxygen atoms because these two elements occupy the same lattice site. However, the dependence of the oxygen concentration on the ammonia flow rate is not so
large. Incidentally, the overall oxygen concentrations in the films investigated here increased from about $4 \times 10^{17}$ up to about $2 \times 10^{18}$ cm$^{-3}$ when the Si concentration was increased from about $3 \times 10^{17}$ to $5 \times 10^{19}$ cm$^{-3}$. Thus, it appears that oxygen incorporation increases as more Si is incorporated into the films. This could be due to the tendency of Si to be oxidized easily.

Although the Si concentration appears to be unaffected by the presence of hydrogen or a change of ammonia flow rate up to certain concentrations (lower than $10^{19}$ cm$^{-3}$), it shows a slight decrease with increased ammonia flow rate when the Si concentration is higher than $10^{19}$ cm$^{-3}$, as shown in Fig. 1(c). This could be due to the formation of silicon nitride when the Si flux is very high. Consequently, this growth condition could result in less atomic Si in the film when the ammonia flow rate becomes higher. However, the amount of change in the Si incorporation is again not very significant considering the amount of Si in the film. Moreover, the Si concentrations as high as that shown in Fig. 1(c) are rarely used in film growth. Thus, it can be concluded that the ammonia flow rate only has a marginal effect on the incorporation of Si, O, and H into Si-doped GaN films grown by the RMBE process, except for small changes in O and Si concentrations when the Si concentration is higher than about $10^{18}$ cm$^{-3}$.

B. Electrical and optical properties

The change of room-temperature electron Hall mobility for the films in set I is shown in Fig. 2. The mobility peaks when 50 sccm of ammonia flow rate is used. The variation of room temperature electron Hall mobility with respect to ammonia flow rate for set II is also shown. The highest electron Hall mobility again occurs at 50 sccm of ammonia flow rate. Therefore, maintaining the optimum ammonia flow rate and/or V/III ratio during the growth of Si-doped films is necessary to obtain films with high electron Hall mobility. This trend matches with x-ray data for the films in set I. Figure 3 shows the variation of the x-ray rocking curve full width at half maximum (FWHM) of the GaN (0002) reflection for set I. The smallest x-ray FWHM value occurs for an ammonia flow rate of around 50 sccm.

Figure 4 shows PL spectra measured at 4.2 K for the three samples in set I. Samples grown with 5, 50, and 73 sccm of ammonia flow rate were chosen as representatives of low mobility on the lower ammonia side, highest mobility, and low mobility on the higher ammonia side, respectively. Bearing in mind the almost constant doping level of the samples, it can be concluded that the FWHM of the exciton bound to neutral donor ($I_2$) transition peak located at about
3.477 eV depends mostly on the film quality. The sample grown with 50 sccm ammonia shows the smallest FWHM value for the 1120 transition peak, which is about 10 meV. Although this value is slightly larger than the value reported for the high quality MOCVD-grown n-type films, a smaller value (about 6 meV) was obtained from thicker (≈3.5 μm) samples grown by the RMBE process under the same conditions.

It is noticeable that the intensity ratio between the 1120 transition peak and the first peak of the donor–acceptor (D–A) pair transition (intensity of I2 peak/intensity of the first D–A pair transition peak) has its highest value for the sample grown with 50 sccm ammonia. For the ammonia flow rate of 73 sccm, the intensity of the D–A pair transition is even greater than that of the 1120 transition. In general, stronger D–A pair transitions for n-type GaN films means lower crystal quality from the specific growth conditions provided by the 50 sccm ammonia flow rate as shown in Fig. 5. The zone axis was slightly off from (1120) zone axis. The microstructure of GaN layer is dominated by extended growth defects as observed previously. Some horizontal growth defects are occasionally visible and the top surface is somewhat facetted and uneven. The top surface became more pyramidal for the films grown with higher ammonia flow rates as shown in Fig. 5(c). This type of morphology has recently been attributed to film growth under nitrogen-rich conditions.

Several TEM works have been reported to correlate the material properties and the microstructures of GaN films grown by various processes. Also, Ruvimov et al. reported that Si doping of GaN improved the structural quality by decreasing the density of threading dislocations and releasing some of the compressive biaxial stress in the film. The cross-section TEM (XTEM) study in this section concentrates on the effect of ammonia flow rate on the microstructure of RMBE Si-doped films. The extended defects originate primarily at the top surface of AlN buffer layer and penetrate through to the top surface of Si-doped layers grown with 5 and 73 sccm of ammonia flow rates as seen in Figs. 5(a) and 5(c). However, density of extended defects abruptly decreased about one order of magnitude (from ~10^9 to ~10^8 cm^-2) at the point (marked with an arrow) where the growth of Si-doped layer was initiated with a 50 sccm of ammonia flow rate as shown in Fig. 5(b). Although some defects were formed within the Si-doped layer, they did not go through the top surface. Therefore, the lower density of extended defects microstructure of Si-doped layer resulted from the specific growth conditions provided by the 50 sccm flow rate.

C. Transmission electron microscopy

Typical cross-sectional bright-field electron micrographs of films grown with 5, 50, and 73 sccm ammonia flow rate are shown in Fig. 5. The images were taken with slightly off from (1120) zone axis. The microstructure of GaN layer is dominated by extended growth defects as observed previously. Some horizontal growth defects are occasionally visible and the top surface is somewhat facetted and uneven. The top surface became more pyramidal for the films grown with higher ammonia flow rates as shown in Fig. 5(c). This type of morphology has recently been attributed to film growth under nitrogen-rich conditions.

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FIG. 3. Variation in FWHM of x-ray rocking curve for (0002) GaN plane of the Si-doped films grown with various ammonia flow rates on highly resistive GaN/AlN buffer.

FIG. 4. Low-temperature (4.2 K) PL spectra of three Si-doped GaN films grown with different ammonia flow rates.

FIG. 5. XTEM images of Si-doped GaN films in set I. The ammonia flow rate used for the growth of Si-doped layer was (a) 5 sccm, (b) 50 sccm, (c) 73 sccm, respectively. The zone axis was slightly off from [1120]. The arrow in (b) indicates the approximate position of the interface between undoped GaN and Si-doped GaN.
of ammonia flow rate could be responsible for the high electron Hall mobility demonstrated by this particular sample.

D. DLTS measurements

The electrical, structural, and optical results are consistent with the trend that a certain ammonia flow rate (50 sccm in this experiment) is required to achieve the highest mobility at the given doping level. It is still not understood how and why this outcome is obtained. One possible explanation could be the difference in the degree of compensation level. When one type of semiconductor is compensated by dopants of the other type or centers with opposite charges, there is a big change in Hall mobility, depending on the compensation level through the scattering mechanism. The compensation ratio could be obtained from a series of simultaneous fitting of experimentally measured Hall mobility and doping level. Recently, a quantitative analysis about donor concentrations, acceptor concentrations and ionization energy of donors was reported for an MOCVD-grown GaN film by carrying out simultaneous fitting of measured mobility and doping level. Another study performed on RMBE-grown GaN films showed that the compensation level is higher (30%–50%) in RMBE samples than in MOCVD samples. However, it is considered that this compensation ratio is too high to be caused only by impurities. On one hand, electrically active crystal defects and/or deep levels created by crystal defects could be a major source of electron scattering at higher temperature. Actually, the concept of electron scattering by crystal defects has been incorporated into other carrier-scattering mechanisms to explain limited room temperature electron Hall mobility values obtained from RMBE samples in Ref. 16.

Although the effect on the carrier mobility might be indirect, the presence of deep levels, regardless of their source, is considered to be affecting the mobility of carriers. Thus, DLTS measurements were performed for Schottky diodes grown with three different ammonia flow rates (20, 60, and 73 sccm) to determine whether there was any relationship between the presence and/or distribution of electron trap states within the band gap and the ammonia flow rate during growth. The ammonia flow rate that gives peak electron Hall mobility demonstrated by this particular sample. The carrier concentrations determined by C–V measurement at 300 K are around \(1 \times 10^{17} \text{ cm}^{-3}\), which are similar to the concentrations, determined by Hall effect measurements. The trap signatures presented in Fig. 7 shows various traps existing in GaN films. The signatures for traps B, C, D, E\(_{a}\), and E\(_{b}\) in Fig. 7 were obtained from MOCVD and HVPE films. Shown together in Fig. 7 is the trap signature for trap C1 found in RMBE GaN films only. The apparent thermal activation energy, \(E_{na}\) and apparent capture cross section, \(\sigma_{na}\) for traps B, C, and D obtained from the MOCVD and HVPE samples used in Ref. 17 are 0.62 eV and 7.4\(\times10^{-15}\) cm\(^2\), 0.45 eV and 1.5\(\times10^{-13}\) cm\(^2\), and 0.24 eV and 2.0\(\times10^{-15}\) cm\(^2\), respectively. The trap C1 seems to be particular for the RMBE-grown GaN films, since it was never reported for the MOCVD- and HVPE-grown GaN films. The \(E_{na}\) and \(\sigma_{na}\) of trap C1 were determined to be 0.44 eV and 1.3\(\times10^{-15}\) cm\(^2\) from the trap signature.

![Fig. 6. Typical I–V curve for the Schottky diodes fabricated from the sample grown with 60 sccm ammonia flow rate.](image)

![Fig. 7. Arrhenius plots of \(T^2/\tau_e\) vs 1000/T for deep levels observed in MOCVD, HVPE, and RMBE-grown GaN Schottky diodes, where \(\tau_e\) is electron emission ratio. The trap signatures for deep levels B, C, D, E\(_{a}\), and E\(_{b}\) were obtained from MOCVD and HVPE samples (see Ref. 17) and C1 from RMBE samples.](image)
The DLTS spectra for the samples are shown in Figs. 8(a) and 8(b) for the two different rate windows. It is clear that, among the three samples investigated, the trap density for C1 level is lowest (less than $1 \times 10^{15}$ cm$^{-3}$ range) for the sample grown with 60 sccm ammonia flow rate. The fact that the sample grown with ammonia flow rate giving the highest Hall mobility also has the lowest densities for C1 trap somehow indicates an effect of deep centers on the transport property. This effect could be second order due to the following two facts. First, the conduction mechanisms through conduction band and deep levels are different. Second, the concentrations of the dopant impurities (in the $1 \times 10^{17}$ cm$^{-3}$ range) is higher than the total trap densities (for example, in the low- to mid-$10^{15}$ cm$^{-3}$ range for the other two samples, measured at temperatures below 380 K).

Therefore, it has been experimentally shown that the presence and density of deep level traps have some influence on the electron Hall mobility of GaN films in conjunction with the ammonia flow rate used during the film growth. However, it should be appreciated that the electron Hall mobility obtained from the Hall effect measurements is the end result of the convolution of many factors such as macroscopic crystalline defects and point defects.

IV. CONCLUSION

Unlike the behavior of impurities in undoped or Mg-doped GaN, the ammonia flow rate seems to have only a marginal effect on the incorporation of impurities into Si-doped GaN films, except for a slight decrease in O and Si with increasing ammonia flow rate when the Si concentration is much higher than $10^{18}$ cm$^{-3}$.

It was found that the electron Hall mobility of Si-doped GaN films grown by RMBE was dependent upon the ammonia flow rate used during film growth. The experimental results reveal that an ammonia flow rate of around 50 sccm gives the highest electron Hall mobility (about 250 cm$^2$/V s) for Si-doped films with about 2 $\mu$m thickness. In addition to the Hall measurements, all the characterization techniques (XRD, low-temperature PL, XTEM, and DLTS measurements) consistently showed that RMBE process requires a certain ammonia flow rate (or V/III ratio if the Ga flux is fixed) to produce Si-doped GaN films with high quality. It was apparent that the density of threading dislocation decreased by about an order of magnitude when a 50 sccm of ammonia flow rate was employed.

From DLTS measurements for Schottky diodes grown with three different ammonia flow rates, one deep trap (C1) specific to RMBE-grown films was found. Furthermore, the concentration of C1 trap and other traps, as obtained by DLTS measurements, was lower in the sample with the highest electron Hall mobility.

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FIG. 8. DLTS spectra measured with rate windows of (a) 20/s and (b) 50/s for the three GaN Schottky diodes grown with three different ammonia flow rates.