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Characteristics of unintentionally doped and lightly Si-doped GaN prepared via pulsed sputtering

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ABSTRACT

We have grown structurally high-quality GaN with a low residual shallow donor concentration (<5 × 10^{15} \text{cm}^{-3}) through pulsed sputtering. Light Si doping to this film with a Si concentration of 2 × 10^{16} \text{cm}^{-3} leads to the formation of an n-type film with room temperature electron mobility of 1240 \text{cm}^2\text{V}^{-1}\text{s}^{-1}, which is comparable to that of the best values for n-type GaN as obtained via conventional growth techniques. At lower temperatures, electron mobility increased, and it reached to 3470 \text{cm}^2\text{V}^{-1}\text{s}^{-1} at 119 K primarily owing to the reduction in the phonon scattering rate. A conventional scattering theory revealed that such high electron mobility in GaN grown via pulsed sputtering can be attributed to the precise control of low-level intentional donors and the reduction in compensating centers. These results are expected to provide significant benefits for future GaN technology by offering high-quality GaN at cost effectively and at low temperatures.

Devices based on the group-III nitride epitaxial films are fabricated thorough metalorganic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE); however, MOCVD and MBE suffer from high growth temperatures (>1000 °C) and low productivity, respectively. These problems limit the availability of nitride devices. We believe that the practical application of nitride devices will become more prevalent once these issues are resolved.

Sputtering technology has been one of the most versatile and commonly used methods for cost effectively preparing a variety of thin films in the semiconductor industry. The sputtering process temperature is much less than that of other processes that do not utilize glow discharge because a high-energy species generated by discharge enhances chemical reactions at substrate surfaces.

Recently, we developed a low-temperature growth technique called pulsed sputtering deposition (PSD), which provides a lower growth temperature for high-quality group-III nitride epitaxial films. This phenomenon is explained if we assume that the pulse supply of film precursors activated in discharge plasma enhances the adatom mobility required to form GaN crystal. Additionally, the PSD allows us to obtain nitride films with a wider range of n- and p-type doping capabilities compared with conventional MOCVD. In fact, the maximum electron concentration achieved through Si doping in GaN was 3.9 × 10^{20} \text{cm}^{-3} with a high electron mobility of 100 \text{cm}^2\text{V}^{-1}\text{s}^{-1}. The minimum resistivity of PSD GaN is as low as 1.6×10^{-4} \Omega\text{cm}, which is the record low value to date. This phenomenon is explained if we assume that bombardment of energetic particles helps introduce dopants in the GaN crystals. Despite these advantages, the basic characteristics of unintentionally doped PSD GaN and lightly Si-doped GaN have not been investigated intensively to date.

In this study, we report the basic characteristics of unintentionally doped PSD GaN with a low residual shallow donor concentration less than 5 × 10^{15} \text{cm}^{-3}. Further, we demonstrate that light Si doping to this high-quality PSD GaN leads to the formation of n-type GaN with very high electron mobility of 1240 \text{cm}^2\text{V}^{-1}\text{s}^{-1}, which is comparable with the best values for an n-type GaN obtained via conventional growth techniques.

We have used semi-insulating HVPE bulk GaN (0001) substrates with a threading dislocation density of 2 × 10^6 \text{cm}^{-2} produced by SCIIOCS Co. Ltd. After degreasing, the GaN
substrates were sequentially dipped into hydrofluoric acid solution (5.2 wt%) and hydrochloric acid solution (36 wt%). Then, the sample was transferred to a pulsed sputtering chamber wherein GaN films were grown at substrate temperatures of 600–700 °C with a sputtering discharge power of 80–100 W. The growth rate was set to approximately 1.5–2 μm/h. The values of the film thickness were carefully determined from calibrated growth rates using optical measurements. Note that the detailed growth procedures have been summarized in the literature.

First, we investigated the basic characteristics of unintentionally doped PSD GaN using photoluminescence (PL) and secondary ion mass spectroscopy (SIMS) techniques. For continuous-wave PL measurements, a HeCd laser (λ = 325 nm) was used as the excitation source. The PL signal was dispersed by a double monochromator (focal length: 0.75 m) with a 1200-groove/mm grating. The dispersed signal was detected by an electronically cooled CCD array. All spectra were calibrated with the emission lines of a mercury lamp. Here the spectral resolution was less than 0.2 meV approximately 3.4–3.5 eV. Figure 1 shows a low-temperature PL spectrum recorded at 15 K for the unintentionally doped GaN grown by PSD. Note that the data for the n-type GaN with Si concentration of $1 \times 10^{16}$ cm$^{-3}$ grown on a bulk GaN substrate by MOCVD are shown for reference. Figure 1 also shows the PL spectrum for the unintentionally doped PSD GaN, free excitons $X_A$ and $X_B$, and neutral donor bound exciton ($D_0$, $X$) emission peaks can be clearly observed at 3.4793, 3.4845, and 3.4721 eV, respectively, and the peak positions of $X_A$ was nearly the same as those of the MOCVD-grown reference sample (3.4791 eV). This indicates that residual stress in the PSD GaN film is comparable to that in the conventional homoepitaxial MOCVD films. Micro Raman scattering spectroscopy was also performed to probe the residual stress in the film. Raman spectra also revealed that the frequency of $E_{2}^{\text{High}}$ mode, which is sensitive to strain, was estimated at 567.4 cm$^{-1}$, which is quite similar to that of homoepitaxial layers grown by MOCVD. The full width at half maximum (FWHM) value was as narrow as 3.4 cm$^{-1}$, which indicates the high structural perfection of the PSD sample. This is consistent with the fact that FWHM values of X-ray rocking curves (XRCs) remain almost unchanged before and after growth of GaN films via PSD as shown in Figs. 2(a) and (b). The XRC FWHM values of 0002 and 10̅12 diffractions were as narrow as 116 and 57 arcsec, respectively. Thus, we conclude that the serious stress or crystalline damage was not induced by ion bombardment during our sputtering process.

The dominant luminescence line of the spectrum for unintentionally doped PSD GaN was assigned as the recombination of free excitons, which is indicative of the low residual impurity level in the PSD-grown GaN. The FWHM values of the $X_A$ and ($D_0$, $X$) emission peaks were as narrow as 2.7 and 1.9 meV, respectively. Note that these FWHM values are the narrowest of the near band edge emission from sputtering deposited GaN films. In addition, our sample showed a strong near band edge emission at 3.4 eV with a FWHM value of 33 meV even at room temperature (RT). This also indicates the high purity and high structural perfection of our sample. SIMS measurements revealed that the residual Si and O concentrations of our sample were less than $1 \times 10^{16}$ cm$^{-3}$ and $5 \times 10^{15}$ cm$^{-3}$, respectively. This is a striking contrast compared to conventional CVD processes, which typically suffer from contamination of Si originating from a quartz reactor. We also note that contamination of transition metals, e.g., Fe, Ti, Ni, and Cr, which are frequently detected in films prepared by sputtering, was not detected with SIMS. It is well known that plasma processes, e.g., sputtering, often causes degradation in semiconductors, e.g., Si. However, these...
results indicate that GaN is more robust against plasma damage and incorporation of undesirable impurities than narrower gap materials. It is likely that this phenomenon can be attributed to the strong chemical bonding between Ga and N, which makes the sputtering process suitable for preparation of device-grade GaN.

To further examine the trace level of the residual shallow donor impurities, we precisely analyzed the position of the (D₀, X) emission and related peaks. The energy separation between Xₐ and (D₀, X) emission peaks was 7.2 meV, which agrees well with the value reported for the O donor.¹¹ Note that additional peaks were observed at 3.4479 eV and 3.4510 eV for the PSD-grown and MOCVD-grown samples, respectively, which are assigned as two electron satellite peaks. The spacing between the (D₀, X) and two electron satellite peaks yielded the donor excitation energy from the 1s to 2s states. For the PSD-grown GaN, the spacing between these peaks was 24.2 meV, which is related to the residual O donors at N sites,¹³ and, for the MOCVD-grown GaN, this value was 21.6 meV, which is related to the Si donors at Ga sites.¹⁴ This is quite consistent with the SIMS results. The combination of PL and SIMS measurements revealed that our sputtering process realizes the growth of high-purity GaN with high structural quality.

The unintentionally doped PSD GaN typically demonstrates highly resistive nature due to low residual shallow donor concentrations and compensation. To investigate the electron transport properties of the PSD-grown GaN, light Si doping was performed systematically in an Si concentration range of 2 × 10¹⁶ cm⁻³ to 2 × 10¹⁷ cm⁻³. The epitaxial film structure and AFM surface image of a typical sample are shown in Fig. 3(a). The isolated layer consisted of 0.1 μm-thick unintentionally doped and 0.2 μm-thick Mg-doped GaN. Then, the Si-doped GaN layers with four different Si doping concentrations and mobilities for samples with varying Si doping concentrations were grown on the isolated layers. The values of film thickness of the Si-doped layers were ranged from 2.2 to 3.4 μm. We found that the surface morphology comprises atomically-flat stepped and terraced structures regardless of Si doping. Here, the root mean surface roughness values were 0.5–0.6 nm. Hall-effect measurements were performed between 77–300 K using a ResiTest 8400 (Toyo Corporation) with a liquid-N₂-cooled temperature-variable sample holder. For van der Pauw geometry, ohmic electrodes (Ti/Al/Ti/Au) were deposited on the four corners of 10 mm × 10 mm sample surface. The temperature dependence of electron concentrations was fit with the charge-neutrality equation assuming a single donor and a compensating acceptor level. Simultaneously, the temperature dependence of the Hall mobilities was also fit according to conventional scattering theory. Matthiessen’s rule was used to estimate the total electron mobility from the individual scattering mechanisms, including ionized impurity scattering, neutral impurity scattering, dislocation scattering, acoustic deformation potential scattering, piezoelectric scattering, and polar optical scattering. The analytical expressions and material parameters used for estimation of these scattering rates are summarized in our previous work. Here, the fitting parameters were donor concentrations (Nₐ), acceptor concentration (Nₐ), and donor activation energy (Eₐ). The obtained values are summarized in Table I. Figures 3(a) and 3(b) show the temperature dependencies of the electron concentrations and mobilities for samples with varying Si doping concentrations. All data can be fit well using a model with the same material parameters. The obtained donor activation energies were reduced from 29.9 to 20.7 meV with increasing Si concentration, which can be explained primarily by Coulombic interaction between ionized donors and Coulomb potential screening by free electrons. The sample with the lowest Si concentration (2 × 10¹⁶ cm⁻³) yielded high electron mobilities of 1240 cm² V⁻¹ s⁻¹ at 295 K, which is comparable to the best reported RT electron mobilities in n-type GaN.¹⁵–¹⁸ Electron mobility increased at lower temperatures, and the peak value was 3470 m² V⁻¹ s⁻¹ at 119 K. To the best of our knowledge, this is the highest value among low-temperature electron mobilities for n-type GaN grown by physical vapor deposition (PVD), such as MBE.¹⁷ Note that MBE yields high-quality GaN films that are comparable to those obtained by PSD; however, the typical MBE technique suffers from low growth rates and high production costs.

Figure 4 shows the temperature dependence of mobilities for samples with various Si concentrations, as well as the theoretical

| TABLE I. Summary of fitting results and peak LT mobilities. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| N_D          | N_A            | E_D             | Peak LT mobility |
| 10¹⁶ (cm⁻³)  | 10¹⁶ (cm⁻³)    | (meV)           | (cm²V⁻¹s⁻¹)     |
| 2.3          | 0.68           | 29.9            | 3470            |
| 6.2          | 1.1            | 25.6            | 2500            |
| 13           | 2.4            | 24.4            | 1920            |
| 24           | 3.6            | 20.7            | 1280            |

Note that MBE yields high-quality GaN films that are comparable to those obtained by PSD; however, the typical MBE technique suffers from low growth rates and high production costs.
fitting curves determined from various scattering rates. As shown in Fig. 4(a), for the sample with the lightest Si concentration, the RT electron mobility ($1240 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) was determined primarily by polar optical phonon scattering, which is the inherent material limit. At low temperatures, the electron mobility was primarily limited by ionized impurity scattering for all samples. Although the scattering rate by dislocations increased slightly with decreasing Si concentration due to the reduction in the screening effect by free electrons, the dislocation scattering was negligible even with the lightest Si-doped sample. Thus, LT mobility could be one of the best criteria for film quality if the dislocation density is sufficiently low. The high LT mobility obtained in this study ($3470 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) can be attributed to precise control of the low Si doping level and the reduction in compensating centers, such as C atoms in N sites, Ga vacancies, and related defects. To obtain higher LT electron mobility, it is essential to reduce impurity concentrations and threading dislocation density. In fact, HVPE-grown n-type bulk GaN with a dislocation density of $5 \times 10^{14} \text{ cm}^{-2}$ yielded record high LT mobility ($7386 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 48 K).  

In conclusion, we have grown high-quality unintentionally doped GaN with a low residual shallow donor concentration (less than $5 \times 10^{15} \text{ cm}^{-3}$) by PSD. Combined PL and SIMS measurements revealed that the O atoms are the main residual impurity in PSD-grown GaN, and their concentration is less than $5 \times 10^{15} \text{ cm}^{-3}$. Light Si doping to GaN films grown by PSD yielded reasonable n-type conductivity, and the sample with Si concentration of $2 \times 10^{16} \text{ cm}^{-3}$ yielded high RT electron mobility of $1240 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. At lower temperatures, the peak electron mobility was $3470 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which, to the best our knowledge, is the highest among the values reported for PVD-grown n-type GaN. This high value can be attributed to precise control of low-level Si concentration by PSD and reduction in compensating centers. These results are expected to provide significant benefit to future GaN technology by offering high-quality GaN with high productivity.

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