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Characterization of undoped and Si-doped bulk GaN fabricated by hydride vapor phase epitaxy

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In this study, the optical, structural, electrical and thermoelectric properties of undoped and Si-doped bulk GaN samples are investigated. The room temperature PL near band emission peaks of undoped and Si-doped bulk GaN samples are 3.414 eV and 3.402 eV. The undoped and Si-doped bulk GaN samples' PL spectra have different defect emission bands which are green band and red band with the maximum at 2.4 eV and 2.0 eV, respectively. At low temperature, the PL spectrum of undoped bulk GaN has well-defined excitonic emission lines, A^0X, D^0X, FX_A (n = 1, 2), while the PL spectrum of Si-doped bulk GaN has just broad emission peaks at the similar energy level. The low temperature PL spectra of both undoped and Si-doped samples clearly show the first, second and third longitudinal-optical phonon (1 LO, 2 LO and 3 LO) replicas. There are no donor-acceptor pairs and electron-acceptors' emission in the PL spectra of the samples. The temperature dependence PL spectra of undoped GaN samples shows that the intensity ratio of the FX_A to D^0X decreases with the increase of the temperature. The full width at half maximum (FWHM) of D^0X emission is about 4.7 meV. The carrier density of the undoped and Si-doped bulk GaN are 4.58×10^{15} and 2.41×10^{18} cm^{-3}, and the mobility of the undoped and Si-doped bulk GaN are 1050 and 286 $cm^2V^{-1}s^{-1}$. The FWHM of (0002) X-ray diffraction rocking curve are 54 arcsec and 95 arcsec for the undoped and Si-doped bulk GaN samples. The power factors of the undoped GaN sample and the Si-doped GaN sample are 0.315×10^{-4}W/mK^2 and 0.35495×10^{-4} W/mK^2, respectively.

1 Introduction The III-nitrides have attracted a great attention for their outstanding martial properties. They have many applications in electronic devices such as high-power, high-frequency and high temperature transistors [1-4]. In addition, III-nitrides have been extensively used for optoelectronics, such as LEDs, LDs, detectors and solar cells [5-8]. Unfortunately, these devices are manufactured mainly by heteroepitaxial methods. The well-known disadvantages of heteroepitaxy are: lattice mismatch, thermal-expansion-coefficient difference and chemical incompatibility, which in effect lead to highly stressed GaN epilayers with high dislocation density and mosaic crystal structure [9]. The growth and characterizations of bulk GaN, which can be used as a substrate for homoepitaxial growth, are highly demanded.

Due to the technological difficulties of GaN growth from the liquid phase, hydride vapor phase epitaxy (HVPE) method has become the first choice for the commercialization of such substrates with its high growth rate and relatively low cost [9-13]. By this method, the formation of freestanding bulk GaN is preceded by the heteroepitaxial deposition of a thick layer of GaN onto an appropriate substrate and a separation step to free the bulk GaN from its substrate. In order to separate the film and substrate a number of techniques, such as mechanical lapping, chemical etching, laser lift-off and void assisted separation, have

been employed [14, 15]. N-type bulk GaN substrate is needed for high power (both optoelectronic and electronic) vertical devices because the carriers can transport to the whole bottom of the device effectively, which improves the power and efficiency of the device significantly. On the hand, high speed lateral devices require the substrate with very low carrier concentration [16]. So the growth and characterization of undoped and Si-doped bulk GaN samples are meaningful.

In this study, the optical, structural, electrical and thermoelectric properties of undoped and Si-doped bulk GaN samples are investigated as determined from photoluminescence (PL) measurements, high-resolution X-ray diffraction (HR-XRD), Hall-effect and Seebeck measurements.

2 Experimental details Undoped and Si-doped bulk GaN samples were grown by hydride vapor phase epitaxy (HVPE) at Kyma Technologies, Inc. The thickness of the undoped and Si-doped bulk GaN samples are about 400μm. The maximum off-cut of the undoped and Si-doped bulk GaN samples are about 0.5°. Both the samples are 10 mm × 10 mm square. Characterizations of the bulk GaN samples were performed on the Ga-face. The structural, optical and electrical properties of undoped and Si-doped bulk GaN samples are investigated as determined from high-resolution X-ray diffraction, photoluminescence measurements and Hall effect measurements.

Variable temperature (8-300 K) PL was employed to assess the optical quality of the bulk GaN samples. Steady-state PL was excited with a continuous-wave He-Cd laser (325 nm) and analyzed with an Acton SP2500 grating monochromator of Princeton Instrument. And the detector is PIXIS-100 CCD from Princeton Instrument. The exposing time is about 500 mS. The accumulation is 10 times. High resolution X-ray rocking curves were measured by a Philips X'Pert MRD system equipped with a four-crystal Ge (2 2 0) monochromator. The instrumental resolution was verified to be better than 10″under this diffraction geometry where the $CuK_{\alpha 1}$ line of X-ray source was used. The slit width of high resolution X-ray is 0.05 mm. The room temperature Hall-effect was measured by an ECOPIA Hall Effect Measurement System using standard Van der Pauw method. Ohmic contacts were formed with 95% indium, 5% gallium droplets on the surface of the GaN samples. The Seebeck measurement procedures are described in detail elsewhere [15]. The Seebeck coefficients were determined by the slope of the graph of Seebeck voltage with a function of temperature difference across the sample, and Seebeck voltages for all samples showed good linearity ($R^2 \approx 0.99$).

3 Results and discussion The optical properties of the undoped and Si-doped bulk GaN are investigated by PL measurements. Figure 1 shows the PL spectra of the undoped and Si-doped bulk GaN measured at room temperature. The room temperature PL near band emission (NBE) peaks of undoped and Si-doped bulk GaN samples are 3.414 eV and 3.402 eV. And it is found that the undoped and Si-doped bulk GaN samples have different defect emission bands which are green luminescence band and red luminescence band with the maximum at 2.4 eV and 2.0 eV, respectively. The full width at half maximum (FWHM) of the defect related peaks of the undoped and Si-doped bulk GaN samples are 500 meV and 560 meV. The green luminescence band of undoped bulk GaN sample is related to charge state of the $V_{Ga}O_N$ complex [17]. The red luminescence band of Si-doped bulk GaN is due to transitions from a shallow donor or conduction band to a deep acceptor level [17].

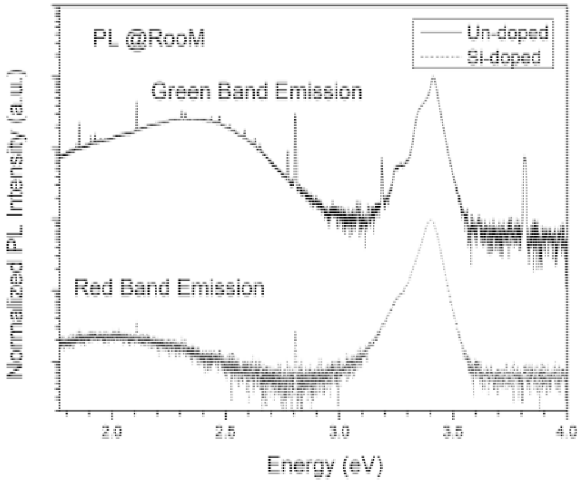

Figure 1 Room PL spectra of undoped and Si-doped bulk GaN samples.

Figure 2 shows the PL spectra of the undoped and Si-doped bulk GaN measured at low temperature (8 K). The low temperature PL the NBE of the undoped bulk GaN sample is dominated by the neutral donor-bound exciton (D^0X) and its first, second and third longitudinal-optical phonon (1 LO, 2 LO and 3 LO) replicas, whose emission are located at 3.474, 3.393, 3.301, 3.209 eV, respectively [18-24]. The FWHM of D^0X PL emission peak is about 4.7 meV. At energy levels smaller than the D^0X, the two-electron transition (TETs) is observed, whose emission is located at 3.454 eV. Free exciton (FX_A) of n = 1 and n = 2 are observed, whose emission are located at 3.481 and 3.498 eV [18]. There are no donor-acceptor pairs (DAPs, about 3.264 eV centered) and electron-acceptors (about 3.288 eV centered) emission in the PL spectra of the samples [18, 25]. Those well-defined exciton emission lines and no DAPs or electron-acceptor emission mean the undoped bulk GaN has a high crystalline quality. For the low temperature PL spectra of Si-doped bulk GaN, the exciton bands in the emission broaden due to the increase of the structural defects. There just one wide NEB peak can be observed at 3.474 eV. Nevertheless, the asymmetry of the main peak is observed clearly. The 1 LO,

2 LO, 3 LO replicas of the NEB peak also can be observed, whose emission are located at 3.370, 3.290 and 3.193 eV, respectively. These results mean that the crystalline quality of Si-doped bulk GaN sample is worse than that of undoped bulk GaN sample. The NEB and its replicas of Si-doped bulk GaN sample have a clear red-shift compare with that of undoped bulk GaN sample.

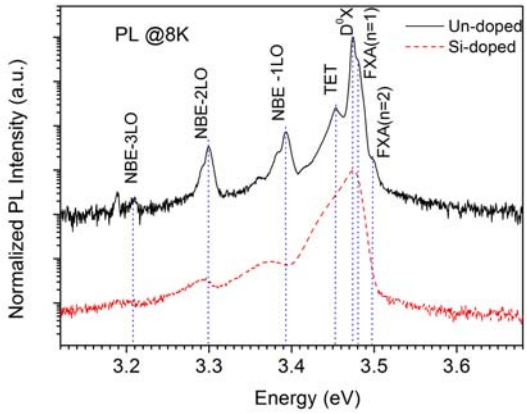

Figure 2 Low temperature (8 K) PL spectra of undoped and Si-doped Bulk GaN samples.

Figure 3 shows the temperature dependent PL spectra of undoped (a) and Si-doped (b) bulk GaN samples in the range of 8 K to room temperature. All the PL spectra intensities are normalized. It is found that the NBE emission of the undoped bulk GaN is formed to be characterized by various excitonic emission lines over the full temperature range. D^0X is the most intense among all the emission at 8.2 K. However, its relative intensity decreases with increasing temperature. Finally, it merges into FX_A. On the contrary, the FX_A emission is much weaker at 8.2 K and its relative intensity increases with increasing temperature. The crossover of those transition mechanism is due to the dissociation of $D^0X \rightarrow FX_A + D^0$ with increasing temperature [18, 21]. The binding energy of FX_A to D^0 is estimated to be 6 meV based on each peak's position. The relative intensity of 1 LO, 2 LO and 3 LO replicas of the NEB peaks decreases with the increase of temperature. The 3 LO replicas of the NEB peak cannot be observed at room temperature. The peak emission at about 3.180 eV is almost unchanged from 8.2 K to 300 K maybe form related with the laser scattering or other unknown peak.

The low temperature dependence PL spectra of the Si-doped bulk GaN sample are different from that of the undoped bulk GaN sample. The D^0X and FX_A emission are mixed over the full temperature. However, the trend of the D^0X intensity decrease with the increase of the temperature can be observed, too. The intensity change of Si-doped bulk GaN sample's replicas is same trend with that of n-doped bulk GaN sample. Only 1 LO and 2 LO replicas of the NEB peak can be observed in the room temperature.

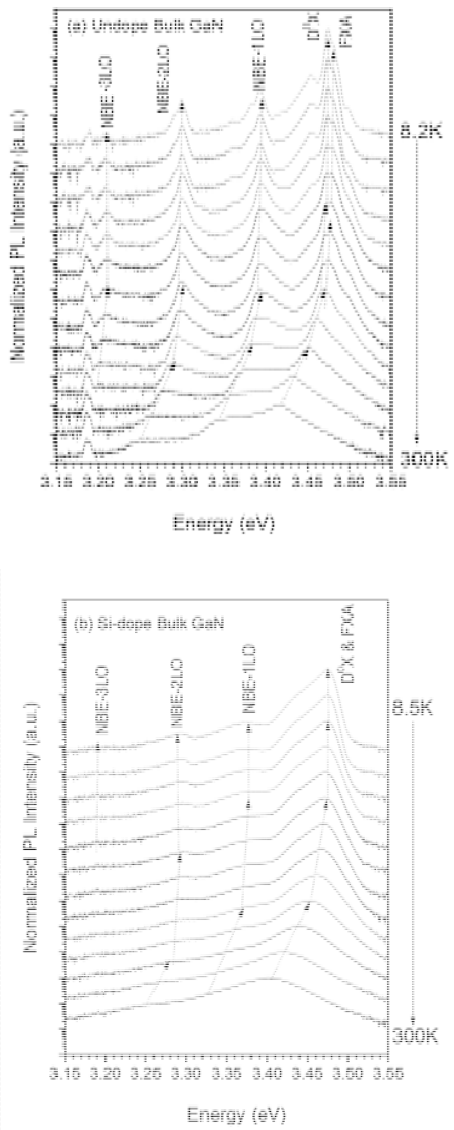

Figure 3 Temperature dependence PL spectra of undoped (a) and Si-doped (b) bulk GaN samples.

Table 1 shows electrical and structural properties for undoped and Si-doped bulk GaN samples. The carrier concentration and mobility of the samples acquire by Hall measurements. The carrier density of the undoped bulk GaN and and Si-doped bulk GaN are 4.58×10^{15} cm^{-3} and 2.41×10^{18} cm^{-3}. The mobility of the undoped bulk GaN and Si-doped bulk GaN is 1050 $cm^2V^{-1}s^{-1}$ and 286 $cm^2V^{-1}s^{-1}$, respectively. The mobility of the bulk GaN samples decreased due to the increase of ionized impurity scattering. The FWHM of the Si-doped bulk GaN samples' XRD rocking curves are increased from 54 arcsec to 95 arcsec, which indicate the degradation of the crystalline quality compared with un-doped bulk GaN sample. The above results are in agreement with the PL discussion.

Table 1 Summary of the electrical and structural properties for undoped and Si-doped bulk GaN samples.

Description	Carrier Density (cm^{-3})	Mobility ($cm^2V^{-1}s^{-1}$)	Conductivity ($\Omega^{-1}cm^{-1}$)	FWHM (0002) (arcsec)
Undoped GaN	4.58E15	1050	0.772	54
Si-doped GaN	2.41E18	286	110	95

The summary of the thermoelectric properties for undoped and Si-doped bulk GaN samples is shown in Table 2. The conductivity of samples is calculated by the carrier density and mobility measured by Hall-effect. The Seebeck coefficient of the undoped GaN sample is -419 μV/K. It is much higher than that of Si-doped GaN sample (-56.7 μV/K). The power factor of the undoped GaN sample is lower than that of Si-doped GaN sample due to the much lower conductivity.

Table 2 Summary of the thermoelectric properties for undoped and Si-doped bulk GaN samples.

Description	Conductivity ($\Omega^{-1}cm^{-1}$)	Seebeck Coefficient (μV/K)	Power Factor ($10^{-4}W/mK^2$)
Undoped GaN	0.772	-419	0.135
Si-doped GaN	110	-56.7	0.354

4 Conclusion In this study, the optical, structural, electrical and thermoelectric properties of undoped and Si-doped bulk GaN samples are investigated. The obvious different properties of undoped and Si-doped bulk GaN samples are discussed in detail. The low temperature PL spectra of undoped bulk GaN have well-defined exciton emission lines and no DAPs or electron-acceptor emission. However, the low temperature PL spectra of Si-doped bulk GaN have mixed exciton emission lines. The FWHM of undoped and Si-doped bulk GaN samples' XRD rocking curves are 54 arcsec and 95 arcsec, respectively. The conductivity of the bulk GaN sample is increased more than two orders of magnitude after the doping with silicon. The power factor of the undoped GaN sample and the Si-doped GaN sample are 0.315×10^{-4} W/mK^2 and 0.35495×10^{-4} W/mK^2, respectively.

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