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Effect of H, O intentionally doping on photoelectric properties in MOVPE-growth GaN layers

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ABSTRACT

GaN crystal growth requires higher purity of materials. Some contaminants in NH₃ gas could be the causal factor of defects in GaN crystals. These atoms act as donor or acceptor. In order to clearly demonstrate the effect of gaseous impurities such as H₂O on the properties of undoped-GaN layer, high purity NH₃ (N70) was used as NH₃ source. The concentration of H₂O in NH₃ was varied at 32, 49, 75, 142, 266, 489, and 899 ppb, respectively. Under the same recipe, we deposited undoped-GaN epitaxial layer with purifier, and H₂O-doped GaN series layers. As similar to the results of CO and CO₂-doped GaN series, the increase tendency of carrier density changing with increasing H₂O concentration. The FWHMs of XRC around (0002) remain stable, witnessing that the crystal quality of GaN layer remain good. LT (15K) PL of undoped-GaN and H₂O-doped GaN were measured, the D⁰X emission peak intensity of all H₂O-doped GaN are decreased drastically compared with undoped-GaN. H₂O impurity was doped into GaN layer, which not only effects electrical properties and but also effects the radiative emission and furthermore effects PL intensity, its mechanism is discussed.

Keywords: MOVPE, GaN, impurities, donors, PL

1. INTRODUCTION

Nitride materials are prospective for optical and electrical devices, GaN as a representative group-III-nitride semiconductor has been applied in light-emitting diodes, laser diodes, and high electron mobility transistors fields in the past twenty years. The preparation of high quality epitaxial GaN film is the most important guarantee for improving the quality of the device. However, problems of crystal defects and unintentional impurities are still remaining, which severely influence GaN crystal and photoelectric property. In the previous study, the species of potential contaminants exist in gaseous sources and their effects on the properties of the epitaxial GaN layer had been discussed. Oxygen, carbon and hydrogen as main unintentional impurity elements were researched^[1-19]. These unintentionally elements in GaN layers could act as donor or acceptor dopants, which may effect the crystal quality, carrier density, carrier mobility and emission efficiency. It is essential to reduce defects and impurities for further improvement of efficiency and reliability. In order to demonstrate the origin of the unintentional impurity elements and eliminate almost all effects on crystal property, some contaminants as primate gaseous source impurities^[1] (shown in Table 1) were intentionally doped in GaN layer, which is an important and difficult work. In the previous research of our group, the effect of oxygen-carbon-containing impurity species CO and CO₂ was analyzed qualitatively and quantitatively.^[2] According to the research result, O as major donor dopant strongly affects the photoelectric properties of epitaxial GaN layer, and carbon incorporation efficiency from CO₂ and CO are lower than oxygen incorporation efficiency. In order to control the carrier density of intrinsic GaN, the impurity concentration of CO₂ in NH₃ must be limited strictly.

Table 1. Primary impurities in NH₃ from three ammonia sources

NH ₃ purity (%)	CO ₂ (ppb)	CO (ppb)	H ₂ O (ppb)	O ₂ (ppb)
99.9995	500	500	500	500
99.99997	50	30	30	30
99.99999	10	10	60	10

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In addition to CO and CO₂, H₂O is also a kind of common oxygen-containing impurity. H₂O as primary hydrogen-oxygen-containing impurity in NH₃ source, its effect on epitaxial layer is not clear. In order to deeply demonstrate the relationship of H₂O dopants and GaN properties, H₂O was intentionally doped into GaN epitaxial layer during MOVPE growth. The moisture level in NH₃ gas could be controlled with using permeation tube. Two kinds of permeation tubes were chosen, moisture concentration can be varied by the operating temperature of the tube. Permeation rate of water vapor had been evaluated before epitaxy experiments by our cooperater T. Teramoto, the results were shown in Table 2. In this work, NH₃ gas with 4.5 slm flow rate was preheated before going into permeation tube cartridge, the pressure in the cartridge was controlled by back pressure regular (BPR). By adjusting the operating temperature, H₂O impurity with various concentration was intentionally introduced into GaN epitaxial layer using MOVPE growth method.

Table 2. Moisture average level in NH₃ (4.5 slm) at different temperature

Low concentration series (short permeation tube)				
Temp. (°C)	50	60	70	
Moisture level (ppb)	32	49	75	
High concentration series (long permeation tube)				
Temp. (°C)	40	50	60	70
Moisture level (ppb)	142	266	489	889

Under the similar recipe, undoped-GaN and H₂O-doped GaN samples were deposited. After epitaxy growth, surface etching procedure was applied for eliminating the effect originated from surface contamination. Step profiler, high resolution X-ray diffraction (HRXRD), room-temperature (RT) hall measurement, and low temperature (LT) photoluminescence (PL) were used to analyze the thickness, crystal quality, electrical property, and optical properties of undoped-GaN and H₂O-doped GaN, respectively. Using van der pauw geometry Hall effect measurement at RT to test the carrier density, carrier mobility and resistivity. The crystal quality of GaN epitaxial layers were analyzed by XRD rocking curve (XRC) around (0002) orientation (Philips X' pert MRD). LT (15K) - PL spectra of epitaxial GaN layers were measured using 325 nm He-Cd laser as excited source, the excited power density was fixed to 0.1W/cm².

2. EXPERIMENTAL PROCEDURE

2.1 Epitaxial growth

Undoped GaN and H₂O-doped GaN thin films were deposited on two inch *c*-plane sapphire wafers in the horizontal MOVPE reactor. High purified ammonia and trimethylgallium (TMGa) were used as Ga and N element sources, respectively. Figure 1 shows the schematic of main gas supply lines and MOVPE reactor, NH₃ flow rate was controlled by MFC, it was fixed to 4.5 slm. NH₃ gas was preheated to arrive at operating temperature before going into permeation tube, in the cartridge, moisture was introduced into NH₃ gas. Pressure of 300 Pa was controlled by BPR. All of the gases including NH₃, N₂ and H₂ were purified to higher level before being introduced into bubbling chamber and reactor.

A LT-GaN buffer layer and a HT-GaN layer were grown on the *c*-plane sapphire substrate in MOVPE reactor, the schematic diagram of the epitaxial GaN layer is presented in Figure 2. H₂O was doped into not only HT-GaN layer but also LT-GaN buffer layer. The undoped GaN layers and H₂O-doped GaN layers were deposited under the similar growth condition shown as Table 3. The concentrations of H₂O were set to 32, 49, 75, 142, 266, 489 and 899, as shown in Table 4.

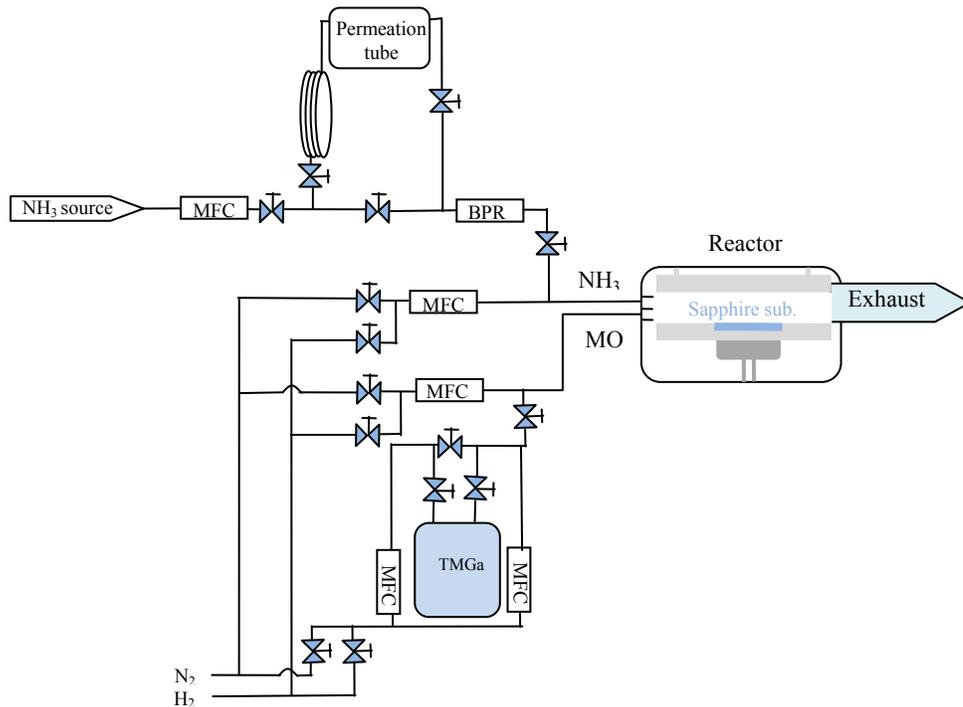


Figure 1 Schematic of main gas supply lines and MOVPE reactor

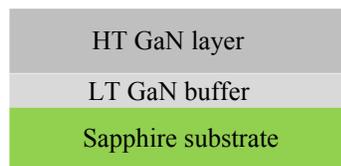


Figure 2 Schematic diagram of the epitaxial GaN layer, the thickness of HT-GaN is around 5 μ m

Table 3. Experiment condition for epitaxial GaN layers.

Layer	T(°C)	Pressure (Pa)	NH ₃	TMGa	V/III
LT-GaN	545	101	4.5	38.25	5255
HT-GaN	1020	101	4.5	52.71	3813

Table 4. Moisture average level in NH₃ (4.5 slm) at different temperature

Impurity type	Impurity concentration (ppb)						
H ₂ O	32	49	75	142	266	489	899

2.2 Etching for surface treatment

Moisture was intentionally introduced into the procedure of MOVPE growth, residual H_2O impurity was accumulated on the surface of the epitaxial GaN layer. The electrical properties of GaN layer was analyzed by Hall measurement, the surface contamination might affect the ohm contact between the electrode material and GaN layer, and then affect the Hall measurement results. The surface treatment was applied for eliminating the effect of surface residual contamination. In this work, we applied dry etching method based on Cl_2 based gases, etching thickness is set to about 100 nm. The dry etching process is not nondestructive, in order to verify the effect of dry etching process on the crystal quality and optical properties, we compared the crystal quality and optical properties of GaN layer before and after etching by XRD and LT-PL, as shown in Figure 3 and Figure 4. Figure 3 shows the XRC orientation around (0002) of undoped GaN layers, two curves present etching and no etching, respectively. Two rocking curves almost coincide, the FWHMs values keep stable.

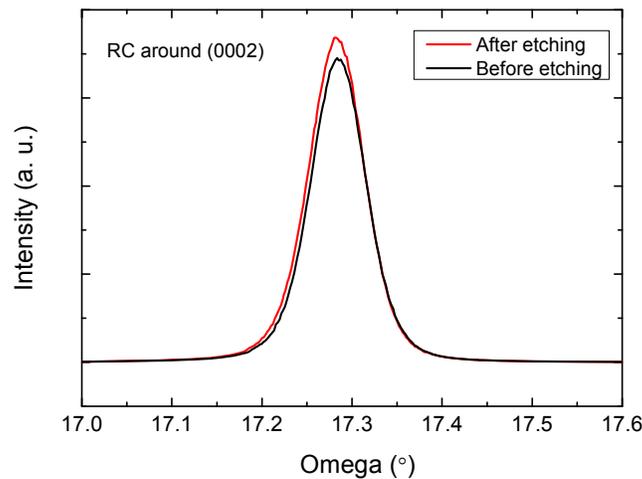


Figure 3 (0002) rocking curves of undoped GaN layers, black color line shows the sample without etching treatment, red color line shows the sample with etching treatment.

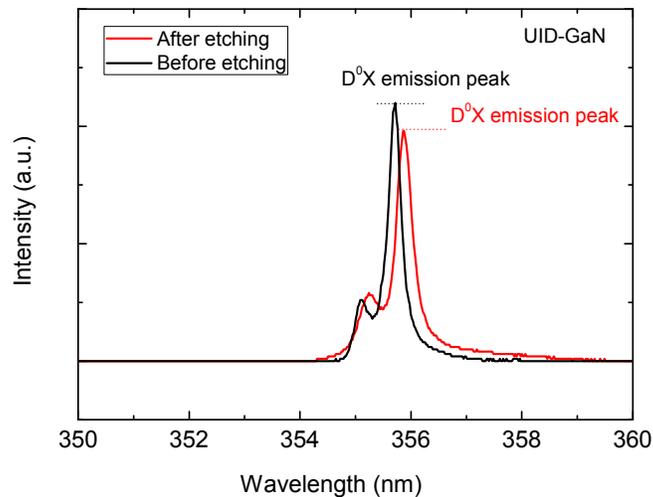


Figure 4 LT(15K)-PL of UID-GaN layers, black color line shows the sample without etching treatment, red color line shows the sample with etching treatment.

Figure 4 shows LT-PL curves of undoped GaN layers with and without etching treatment. Compare to the LT-PL of no etching sample, the change of etching sample's D⁰X emission peak wavelength and intensity is not obvious. So etching for surface treatment is conducive to remove the surface contaminants and keep good crystal quality.

3. RESULTS AND DISCUSSION

3.1 Crystal quality

FWHMs values of XRC orientation around (0002) were used to reflect the crystal quality of the undoped GaN and H₂O-doped GaN. All of the samples including undoped GaN and H₂O-doped GaN were analyzed after etching for surface treatment. Figure 5 summarizes the FWHMs results of the XRC around (0002) for the all samples, the FWHMs values are all focus around 270 arcsec. The FWHM remains constant at lower H₂O doping concentration (≤ 899 ppb), witnessing that the crystal quality of GaN layers remain good at these doping level, as observed previously in research on CO and CO₂-doped GaN by our group.^[2]

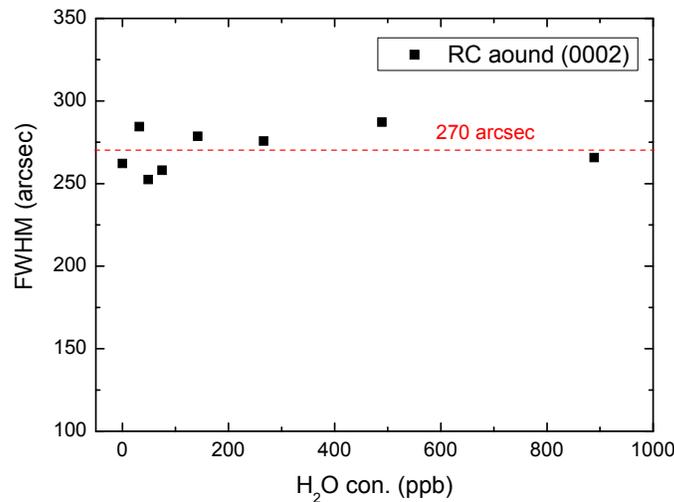


Figure 5 FWHMs of (0002) rocking curves tendency exist in H₂O-doped GaN with different impurity concentration.

3.2 Electrical properties

The 5×5 cm² GaN samples were fabricated to test electrical properties using van der pauw geometry Hall effect measurement at RT. All of the samples show n-type conductivity that are similar to those of the CO and CO₂-doped GaN layers.^[2] The carrier density values of undoped GaN and H₂O-doped GaN were compiled into the graph that summarizes the changes in the carrier density values with H₂O impurity concentrations, shown in Figure 6. The carrier density of undoped GaN sample is 1.8×10¹⁶ cm⁻³, with H₂O impurity concentrations increasing, the carrier density increases. Oxygen derived from H₂O should be shallow donors at N sites, which results in the increasing of carrier density. The increasing tendency of H₂O doped GaN is similar to CO-doped GaN.

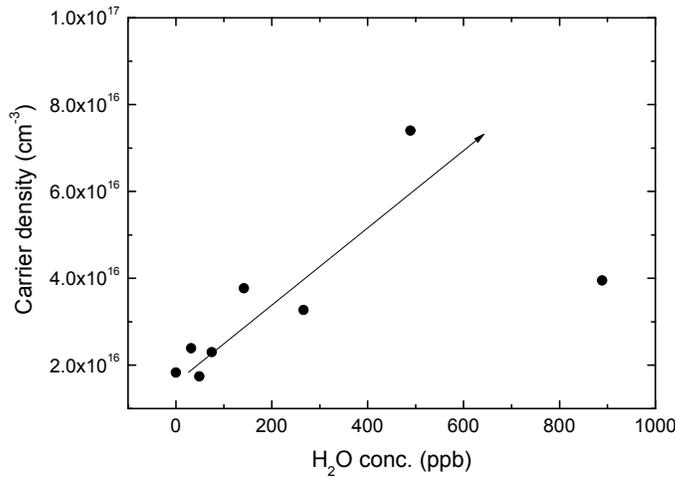


Figure 6 Carrier density curves of H₂O-doped GaN films with various H₂O impurity concentration changing from 35 ppb to 899 ppb in NH₃.

3.3 Optical properties

LT (15K)-PL spectra were tested to demonstrate the impurity, defect, and optical properties. The D⁰X emission peaks were observed to dominate the LT-PL spectra for undoped GaN and H₂O-doped GaN, as shown in Figure 7. The intensity of D⁰X emission peak is more sensitive to H₂O doping, which decreases dramatically with H₂O doping. A small amount of H₂O doping is enough to strongly influence D⁰X peak emission, it is different to CO and CO₂ doping. Hydrogen impurity can have different valence (H⁰, H⁺, H⁻) values in the GaN layer, which affects photoelectric properties of GaN layer.^[9-14] Hydrogenated states (H) existing, resulting in a non-radiative process, which weakening the radiative emitting.^[19] H₂O impurity existing in GaN layer, which not only effects electrical properties and but also effects the radiative emission and furthermore effects PL intensity.

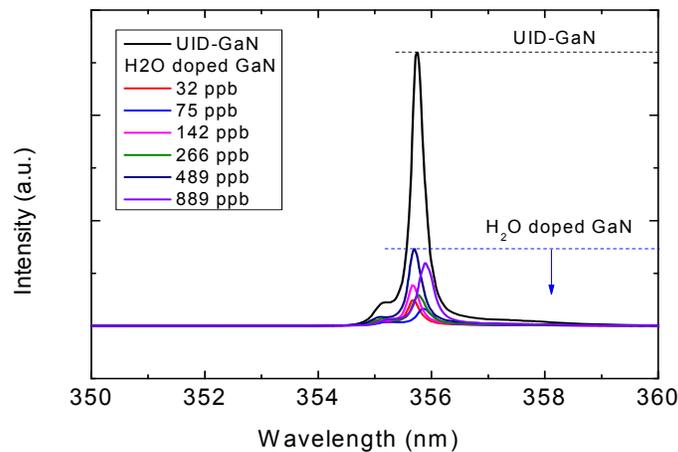


Figure 7 LT (15K)-PL spectra of undoped-GaN and H₂O-doped GaN samples, the black broken line indicates the intensity of D⁰X emission peak of undoped GaN

4. CONCLUSION

H₂O as main NH₃ source impurity was intentionally doped into the epitaxial GaN layer. Crystal quality remains well with lower H₂O doping concentration (< 899 ppb). The increase tendency of carrier density changing with increasing H₂O concentration. The LT(5K) D⁰X peak intensity of all H₂O doped GaN are decreased drastically compared with undoped GaN. Hydrogen impurity existing in GaN layer, which not only effects electrical properties and but also effects the radiative emission and furthermore effects PL intensity. The degradation of the optical properties of GaN layers is more sensitive to the presence of H₂O as an impurity than to CO and CO₂.

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