Plasma-Induced Damage of GaN and Its Recovery by Atomic Hydrogens at a Room Temperature

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1. Introduction

Gallium nitride (GaN) has emerged as the most promising material for various potential applications in optical and high-power electronic devices, because of its wide band gap energy of 3.4 eV, high thermostability, and high electron mobility. In industrial device fabrications, there are demands for GaN etching techniques keeping the smooth surface and realizing low defects, and highly selective etch over some materials, such as AlGaN. Conventionally, the plasma etch would create point defects in crystal and etching residues on the surface as resulted from the ion bombardment and the chemical reaction with reactive species. Those damages would degrade electrical performances by increasing the current leakage and lowering the breakdown-voltage. Thus, a post-process of the plasma etch has been greatly concerned in the recovery of induced damages of GaN for improving its electrical behavior.

Lee et al. reported that the creation of lattice-defects in GaN occurred during a nitrogen plasma treatment. They proposed that it was caused by the bombardment of energetic nitrogen ions [1]. Cao et al. tried to recover these damages by employing a rapid thermal anneal in N_2 , however they issued a problem that nitrogens were preferentially desorbed at high temperatures (above 900°C) [2]. Hence, it needs to develop a novel post-process of GaN materials subjected to plasma processes and we propose a method without ion bombardments and heating up at high temperatures.

In this study, we have demonstrated the recovery treatment of plasma-induced damages on GaN films with high-density atomic H (H* radical) at a room temperature, hereafter called the "H* radical anneal". After the treatments, we have evaluated the properties of the GaN using photoluminescence (PL) for optical characteristics, in-situ X-ray photoelectron spectroscopy (XPS) for the stoichiometric composition of surface, and ex-situ atomic force microscopy (AFM) for surface morphology.

2. Experiments

Epitaxial GaN film was deposited and doped with Si (concentration at 10^{16} cm⁻³ level) by a metal organic chemical vapor deposition (MOCVD) with thickness of 2 μ m on a sapphire substrate. Undoped buffered layer between the sapphire substrate and the epitaxial layer was formed with thickness of 25 nm.

The Cl₂ plasma, as shown in left of Fig.1, was generated by sustaining 13.56-MHz radio frequency (RF) power to the internal-type low-inductance antenna [3]. The plasma was separated from the irradiation chamber by acceleration electrode with eight 0.7-mm-diameter holes. The ion energy and flux was controlled by electrical potentials applied to the acceleration and focus electrodes. Simultaneously, radicals diffused from the plasma and irradiated to the sample in the chamber. A Faraday-cup at the identical position of the sample was used to measure the actual ion energy and ion flux. Typical pressures of the plasma source and the irradiation chamber was 0.8 Pa and 6 $\times 10^{-3}$ Pa, respectively.



Fig. 1 Experimental setup.

First, GaN samples were cleaned by immersing in 2% hydrofluoric acid (HF) for 1 min and in 17.5% hydrochloride acid (HCl) for 1 min to eliminate native oxides and metallic contaminants. Next, the samples were immediately introduced to the chamber and exposed to the energetic ion beam with an energy of 500 eV extracted from the chlorine plasma. The Ion dosage was 5×10^{16} cm⁻².

Subsequently the H* radical anneal at a room temperature was carried out in next chamber equipped with the source of high-density hydrogen atoms, namely the high-density radical source (HDRS). Details of this source have been published elsewhere [4].

Samples were evaluated its stoichiometrically compositional change by the in-situ XPS measurement with Mg K α X-ray (1253.6 eV) source and the take-off angle at 90°. Signals of Ga 3d at binding energy of 18.6 eV, N 1s at 397.0 eV, Cl 2p at 201.0 eV, and O 1s at 531.0 eV were measured. Ex-situ PL measurements with excitation lights



Fig. 2 PL intensity taken at room temperature for samples: as-grown, as etched, and H* annealed GaN samples.

of a He-Cd laser (325 nm) were made to evaluate optical properties. Illuminated areas were with 1 μ m². The surface morphology was measured by AFM with a cantilever made of SiN in tapping mode.

3. Results and discussion

Figure 2 shows a comparison among the band-edge (362 nm) PL intensities of n-GaN: as-grown, etched, and then H* annealed samples taken at room temperature. The PL intensity decreased dramatically after the energetic ion irradiation process. This clearly indicated that the collision cascade of ion bombardments created defects in the bulk of GaN. Those defects were significantly improved in PL intensity by the H* annealing by passivation of the defect in the GaN bulk.

Figure 3 shows compositional changes of surface of GaN samples. The plasma source's inner wall made by quartz was etched to emit oxygen, so that Cl (triangle) and O (circle) were major residues, and the compositional ratio of oxygen (O) was increased to about 42.0 %. By detailed analysis for Ga 3d (peak located at 19.9 eV arisen from Ga-N bonds), as-grown GaN surface exhibited almost stoichiometric composition of Ga:N = 1:1. For the as-etched samples, chemical shifts (peak at 20.5 eV for Ga-O bonds) were observed. The N/Ga ratio underneath of the residues such as Cl and O were increased to 47.5% for



Fig. 3 Atomic composition of N, Ga, Cl, O in as-grown, etched and H* recovered GaN samples.



Fig. 4 X-ray Photoelectron Spectra of Ga 3d in as-grown, etched, H* recovered samples.

as etched samples. It points out that N was preferentially desorbed and the surface was resulted in the Ga-rich.

After 5-min H* anneal at a room temperature, Cl residues were completely removed and abundant O was also reduced. They probably were both bonded physically to the surface with weak Van der Waals forces, and can react with the H atoms, followed by the production of reactions as HCl and HClO, which are volatile.

Moreover, the metallic Ga peak (binding energy at 18.6 eV) was increased after H* anneal as shown in Fig.4. The active H* diffused in and broke the Ga-N bonds, once the N bond was desorbed, N vacancy and free Ga was formed. Subsequently, the free Ga migrated and agglomerated to the metallic Ga on the GaN surface. This migration might realize the smooth surface with low root-mean-square (RMS) roughness of 0.521 nm after the H* anneal. It suggests that the H* anneal is also efficient to restore the surface morphology.

4. Summary

The optical characteristics, stoichiometry, and morphology of Cl_2 plasma beam etched n-GaN before and after H* radical anneal at a room temperature were investigated by PL, XPS and AFM. The H* anneal was efficient process of removing the etch residues comprising of Cl and O. Recovery of the stoichiometry and smoothness of morphology properties of GaN surface were achieved. In particular, the H* passivation to the lattice defect in the bulk of GaN was confirmed by improving the PL intensity at edge-band.

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