Gas-source MBE growth of GaN films using tertiarybutylhydrazine as a nitrogen precursor

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Abstract

As a wide band-gap semiconductor, III-V nitrides have long been recognized as a useful material developing blue and ultraviolet optoelectronic devices. The high stability of ammonia, which requires high growth temperature in standard group III nitride metal-organic vapor-phase epitaxy (MOVPE), stimulates the search for alternative nitrogen precursors. GaN epitaxy at lower temperature was achieved by using hydrazine or hydrazine derivatives, such as monomethylhydrazine and dimethylhydrazine. These materials decompose at lower temperatures than ammonia, but introduce carbon impurity in the epilayer [1] and are with carcinogenic nature.

Tertiarybutylhydrazine (TBHy), one of the hydrazine derivatives, is a relatively safe material (noncarcinogenic). In addition, it may be able to realize a low carbon incorporation in GaN films due to the chemical properties of TBHy, which is similar to GaAs growth with TBAs. We thus have proposed TBHy as an alternative nitrogen precursor to ammonia for nitride growth at low temperature, and achieved single crystalline GaN films on sapphire(0001) by MOVPE and gas-source molecular beam epitaxy (GSMBE) [2,3].

In this study, growth behavior of GaN by GSMBE using TBHy was investigated by in-situ reflection high-energy electron diffraction (RHEED).

To obtain high quality GaN, it is well known that nitridation of sapphire substrates and/or two-step growth with a low temperature buffer layer are essential techniques. At first, we have attempted the nitridation of sapphire(0001) by TBHy. In-situ RHEED patterns changed at the substrate temperature (T_g) of 900 ℃, TBHy pressure (P_{TBHy}) of 5.0×10^{-5} Torr, and the irradiation time above 10 min. RHEED studies showed that the mismatch of reciprocal rod spacing with respect to that of the sapphire surface saturated around -12%. This value is very close to the expected mismatch between AlN and Al_2O_3 (-11.2%). Moreover, from the result of Auger electron spectra, Auger signal intensity of N_{KLL} peak was detected on TBHy-irradiated sapphire surface. These results indicate that the formation of an AlN_x layer was formed when the sapphire substrate is exposed to TBHy, which indicate nitridation of sapphire substrate by TBHy.

We have also studied deposition condition of low-temperature GaN buffer layer on nitridated substrates. From the RHEED studies, amorphous-like layer was obtained at T_g of 400 ℃, P_{TBHy} of 5.0×10^{-5} Torr, and Ga beam equivalent pressure (P_{Ga}) of 5.0×10^{-8} Torr.

The two-step growth of GaN films using TBHy under the different growth conditions were carried out. The results of atomic force microscopy (AFM) observation are shown in Fig. 1. Relatively smooth surface with large GaN islands was obtained when two-step growth procedure followed by the surface nitridation was adopted. From the results of RHEED, crystal structure of GaN epilayers was influenced by P_{TBHy} and T_g as indicated in Fig. 2.

The RHEED pattern for GaN epilayer at lower P_{TBHy} of 2.0×10^{-5} Torr indicates that a hexagonal phase GaN (h-GaN) was dominantly grown [Fig. 2(a)]. In the case of the growth at higher P_{TBHy} of 5.0×10^{-5} Torr, however, the pattern corresponding with the cubic phase GaN (c-GaN) was obtained [Fig. 2(b)].

C-GaN was formed by increasing the TBHy flux (V/III ratio) as well as the substrate temperature. These tendencies, however, were very different from previous reports [4,5]. It is considered that some of pyrosites which generated by thermal decomposition of TBHy on the growing surface may disturb the steady

state growth conditions.

In conclusion, we obtained h-GaN and c-GaN by controlling the growth conditions in the GSMBE with TBHy as a nitrogen source.

References

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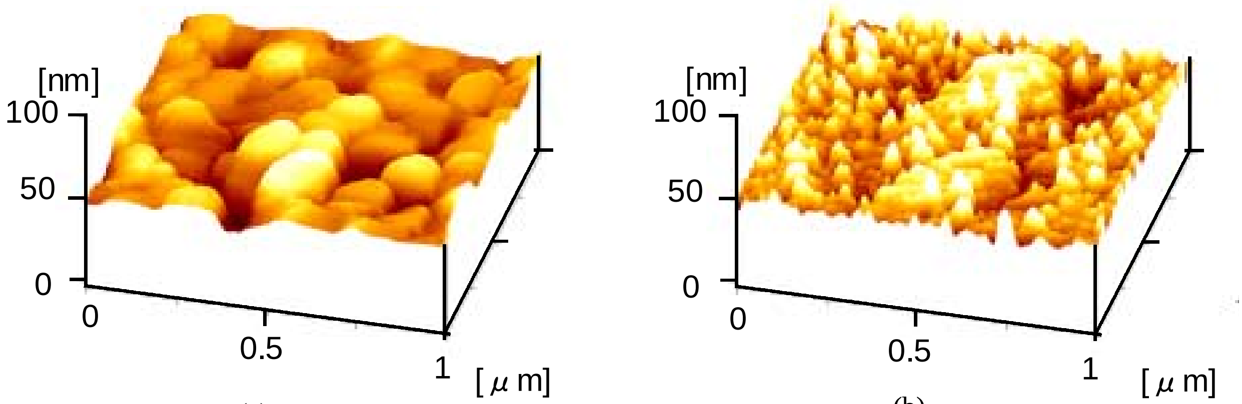
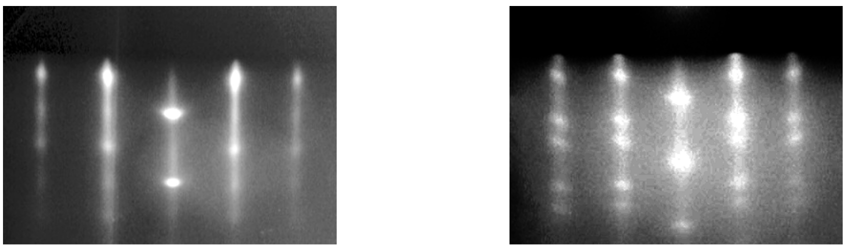


(a) (b)

Fig. 1. AFM images for h-GaN epilayers grown on the annealed buffer layers (a) with and (b) without the substrate nitridation. Ga flux, P_{TBHy}, and T_g for epilayers were 3.0×10^{-7} Torr, 2.0×10^{-5} Torr, and 700 ℃, respectively.



(a) (b)

Fig. 2. RHEED patterns after two-step growth of GaN at P_{TBHy} of (a) 2.0×10^{-5} Torr (hexagonal phase), (b) 5.0×10^{-5} Torr (cubic phase). Ga flux and T_g for epilayers were 3.0×10^{-7} Torr and 700 ℃, respectively.