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HVPE법에 의한 질화갈륨 단결정막 성장시 상전이에 관한 연구

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Phase Transformation in Epitaxial Growth of Gallium Nitride by HVPE Process

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요 약

HVPE(Halide Vapour Phase Epitaxy) 법에 의하여 육방정계 질화갈륨(GaN) 단결정막의 (0001)면에 섬모양으로 배향된 입방정계 β-GaN를 성장시켰다. 입방정계 β-GaN상과 육방정계 α-GaN상 사이의 상호 배향은 $[1\bar{1}0](111)$ β-GaN//$[11\bar{2}0](001)$ α-GaN 관계를 갖는 것으로 관찰되었다. 삼각섬 모양을 한 β-GaN는 막 표면에 평행인 (111) 면에 대한 쌍정위치를 점하고 있었다. 광발광(PL) 및 국소부위 음극선 발광(CL)을 측정하여 β-GaN의 금제대폭 값은 실온에서 3.18±0.30eV로 얻어졌다.

Abstract

The oriented islands of cubic gallium nitride are grown on the (0001) surface of hexagonal GaN epitaxial films by halide vapour phase epitaxial process.

The mutual orientation of cubic β-GaN and hexagonal α-GaN phases was observed as : $[1\bar{1}0]$ (111) β-GaN//$[11\bar{2}0]$ (0001) α-GaN. Trigonally faced islands of β-GaN occupy the twinned positions in relation to (111) plane in parallel to the film surface. The band gap value for β-GaN determined from photo- and local cathodoluminescent measurments is estimated to be 3.18 ± 0.30 eV at room temperature.

1. Introduction

Gallium nitride films are intensively investigated due to their prospective application to light emitting diodes (LED)[1]. Gallium nitride usually crystallizes in a wurtzite type, α-GaN, with lattice parameters of a=3.18Å and c=5.16Å. Cubic modification β-GaN of sphalerite type, a_o=4.49-4.51Å, is unstable[2]. Theoretically β-GaN is more suitable than the hexagonal one as to the usefulness for LED-devices, since the cubic crystal lattice is isotropic, and hence rather susceptible to the impurity doping [3]. It is well known that the cubic semiconductor compounds of sphalerite structure can be easily doped by the impurities of different kind, while the doping of α-GaN is rather difficult. Some recent publications report the growth of β-GaN films on the cubic substrates [4~8]. The β-GaN epitaxial films have been grown by plasma assisted molecular beam epitaxy on β-SiC[4], (001) Si[5], GaAs[6~7] and (001)MgO[8]. TEM-investigations revealed that the structural defects in these films are caused by the lattice mismatch between the films and the substrates.

It was noted earlier[9] that during halide vapor phase epitaxial deposition (HVPE) the fluctuations in the growth parameters or the attendance of uncontrolled impurities often caused appearance of some peculiar morphology on the (0001) α-GaN surface, this being attributed to the precipitations of cubic β-GaN crystallites.

In the present study further investigations are attempted into the structure, morphology and photoluminescence as well as cathodoluminescence properties of gallium nitride films grown on the (0001) Al_2O_3 substrates by HVPE. The twinned trigonal-shape islands of β-GaN are found on the surface of as-grown (0001) α-GaN films, when the steady-state growth conditions are disturbed by the sharp decrease of HCl-feed rate in its gas flow stream and simultaneously by the decrease of the growth temperature. According to Ref.[10], the appearance of the cubic β-GaN is explained by the formation of stacking faults in the wurtzite lattice due to small difference between the free energies for the formation of the wurtzite and zinc blende types of crystal structures.

2. Experiment

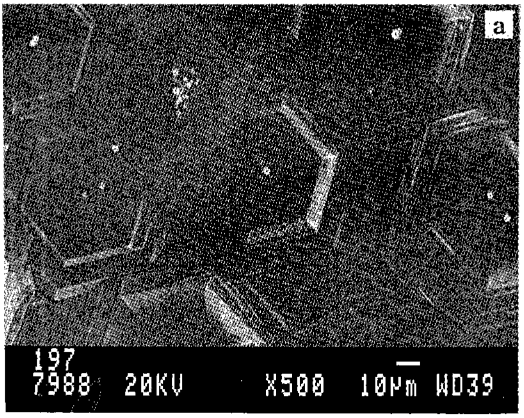
The growth of α-GaN films was carried out in an HVPE reactor under the conditions similar to those described elsewhere [11]. The polished (0001) Al_2O_3 substrates were etched in the acid mixture of ($3H_2SO_4$ + H_3PO_4) at 280-300 ℃ and washed in distilled water. Steady-state growth conditions were disturbed by the marginal decrease in HCl flow rate so as to cease the growth of the α-GaN layer. Simultaneously, the temperature of the substrates was lowered. The morphology of the resulting films was studied by scanning electron microscope (JSM-840), the structure and phase identification by reflection high energy electron diffraction (RHEED) at accelerating voltage of 75 kV, and photoluminescence (PL) spectra by a spectrometer (Jobin-Yvon HR-640) with a continuous wave He-Cd laser of 325 nm (Liconix). Local cathodoluminescence (CL) spectra were measured by scanning electron microscope (JSM-2). The sample area for analysis could be scanned from 10^4 to 10^{-2} ㎛^{2}, the spectral resolution being of 3 meV.

3. Results and Discussion

3-1. The morphology of gallium nitride films grown on (0001) Al_2O_3 substrate under steady-state and unsteady-state conditions

The GaN films grown under the steady-state conditions (substrate temperature = 990-1010℃, gallium temperature = 900℃, HCl flow rate = 6.7 sccm, NH_3 flow rate = 2 SLM, and He-carrier flow rate = 1.8

SLM) revealed the growth of the usual hexagonal pyramids on the sapphire surface (Fig. 1a). The hexagon sides were directed along the <1010>, the lateral faces of pyramids were in parallel to {1014} planes or to {1011} planes. The sharp decrease in HCl flow rate and the lowering of the substrate temperature in the growth zone resulted in the formation of trigonal-shape islands (Fig. 1b). Interestingly, they are turned around to each other by the angle of 180° . The sides of the trigonal deposits are in parallel to those of hexagonal pyramids, their lateral faces being of the extended flat areas and macrosteps. One can see the droplet-like precipitations on the top-most surface of the trigonal deposits. These morphological features imply that the GaN films grown at unsteady-state conditions (HCl conc. and temperature gradients) consisted of two phases, viz. hexagonal α-GaN and cubic β-GaN.



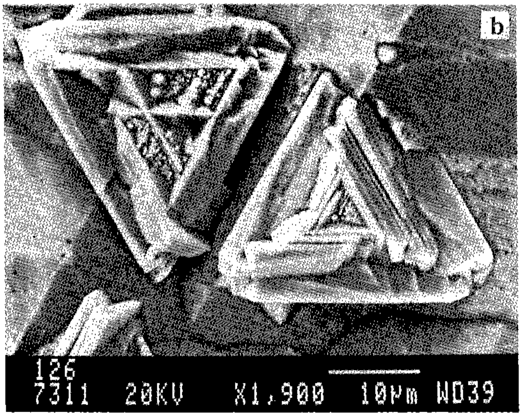


Fig. 1. The morphology of GaN films grown on (0001) Al_2O_3 (a) as-grown film of single phase structure (hexagonal wurzite-type) and (b) as-grown film of mixed-phase structure (hexagonal wurtzite- and zinc blende types).

3-2. RHEED study on phase composition and structure of GaN films

RHEED patterns from the surface of gallium nitride films grown under steady-state and unsteady-state conditions are presented in Fig. 2(a-d). When the incident electron beam was in parallel to <10$\bar{1}$0> directions, the RHEED patterns became similar for both cases, Fig. 2a and c. If the incident electron beam was in parallel to <11$\bar{2}$0> directions, the RHEED-patterns were markedly different (Fig. 2 b-d) ; that was, numbers of additional systematic reflections were presented in Fig. 2d, as compared to Fig. 2b. The RHEED-patterns are interpreted as shown in Fig. 3, and the interplanar distances (d_{hkl}) for α-GaN and β-GaN are presented in Table 1. The geometry of diffraction patterns was

Table 1. The interplanar distances for α- and β-phase GaN.

Hexagonal		Cubic	
d, Å	hkl	d, Å	hkl
2.760	10.0		
2.590	00.2	2.592	111
2.430	10.1	2.245	200
1.884	10.2	1.587	220
1.591	11.0		
1.461	10.3		
1.382	20.0		
1.357	11.2	1.354	311

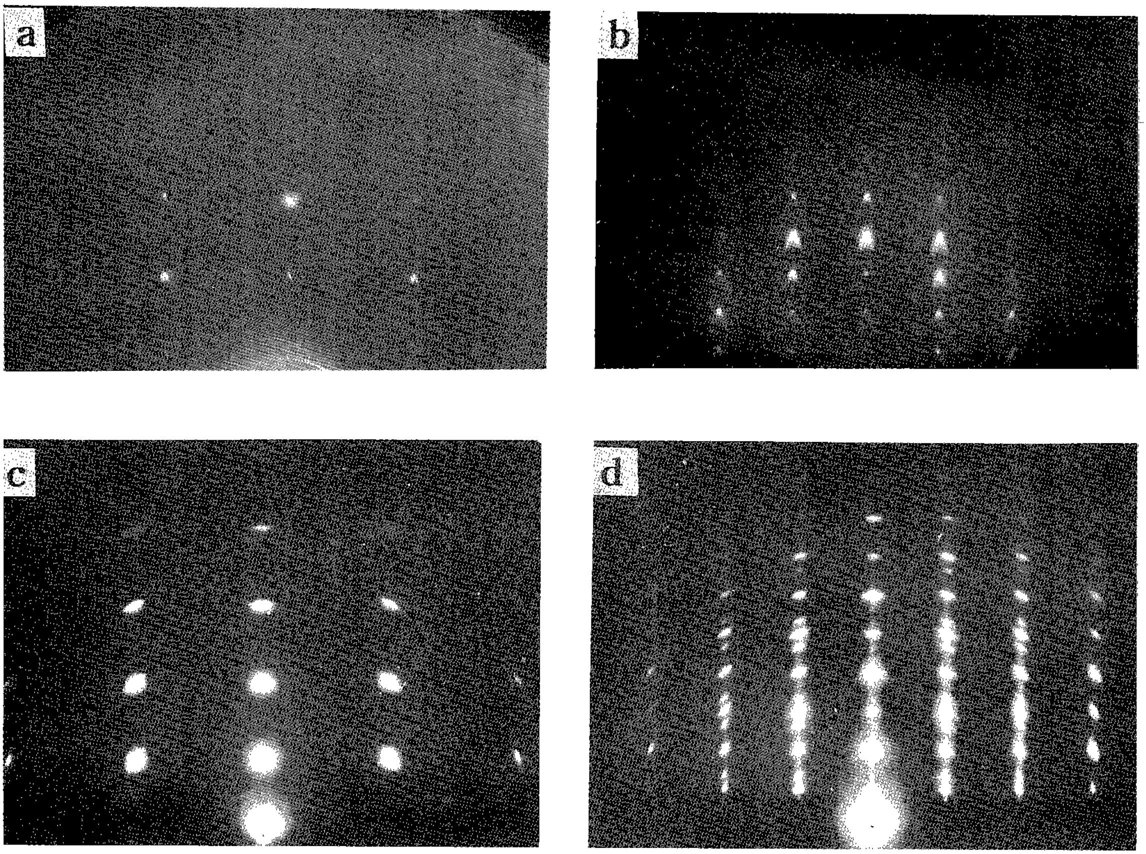


Fig. 2. RHEED patterns from film surface of hexagonal phase (a,b) and two-phase (cubic and hexagonal) (c,d) films; (a) and (c) - <10$\bar{1}$0> azimuth and (b) and (d) - <11$\bar{2}$0> azimuth.

similar, dhkl values being of very close proximity for hexagonal and cubic phases of gallium nitride in the <10$\bar{1}$0> and <11$\bar{2}$ > azimuths, respectively (Fig. 3 a, b). Thus, the presence of β-GaN in the (0001) surface of α-GaN can not be distinguished in these azimuths. RHEED-patterns taken in <11$\bar{2}$0> direction are more complicated but being informative about two structure modifications of gallium nitride.

Now, it may be pertinent to discuss the diffraction pattern scheme of Fig. 3c in some details. It presents three superimposed diffraction patterns: one from α-GaN, <11$\bar{2}$0> azimuth (small black circle) and the other two from β-GaN, <1$\bar{1}$0> azimuth. The reflections from the cubic phase form two similar nets, as denoted in empty circles and squares, each being positioned in opposite directions by rotating around [111]-axis by the angle of 180° . The RHEED-patterns allows one to conclude that the hexagonal and cubic phase of gallium nitride coexisted on the surface in the crystallographic orientation as : [110] (111)β-GaN // [1120] (0001)α-GaN. The cubic gallium nitride islands are twinned in relation to (111) plane. This result is in a good agreement with the morphological data (Fig. 1b).

3-3. Luminescence

The luminescent properties of the specimens were observed by means of photoluminescence (PL) and local cathodoluminescence (CL) measurements. Fig. 4 shows the

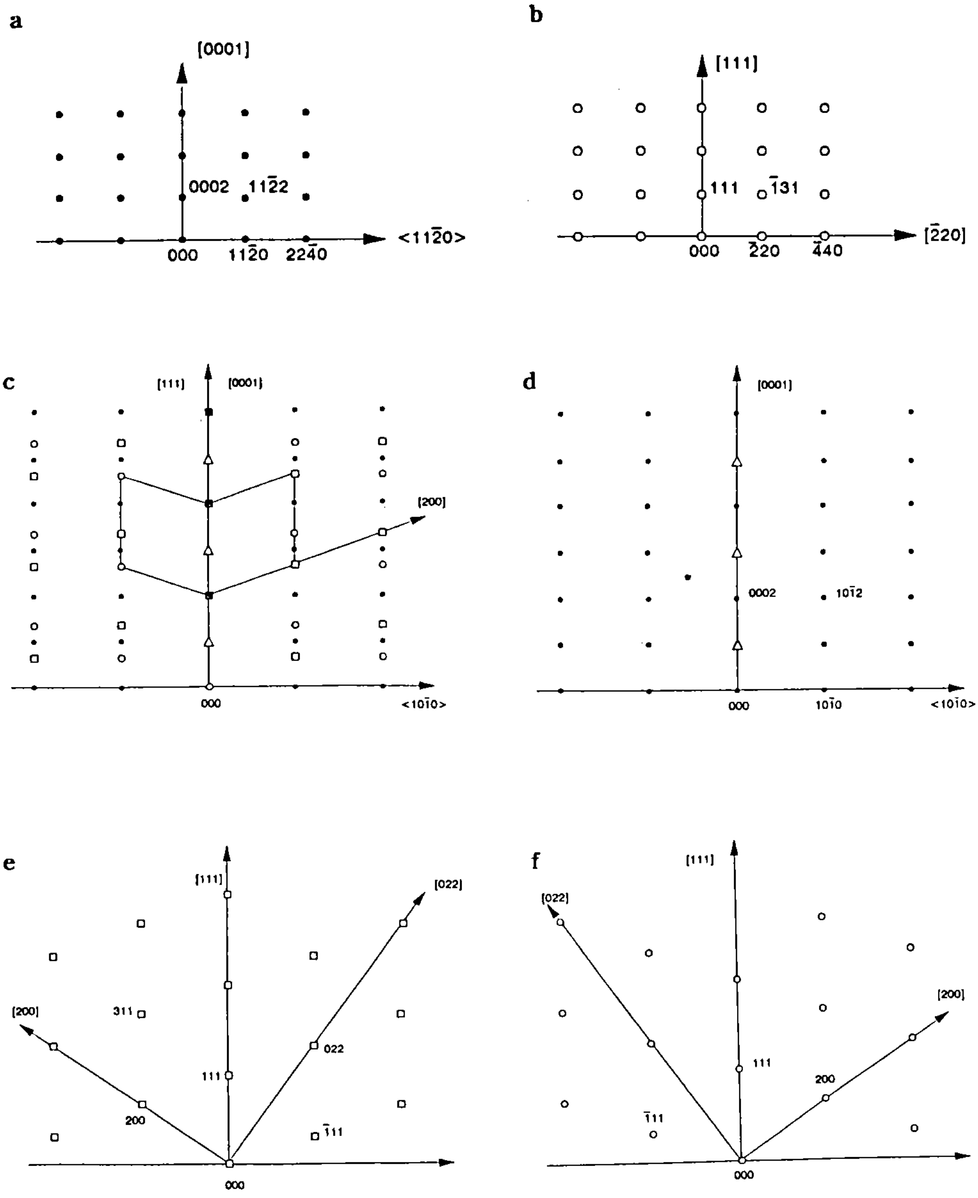


Fig. 3. Schemes of RHEED-patterns for hexagonal and cubic GaN :
(a) hexagonal, $\langle 10\bar{1}0\rangle$ azimuth; (b) cubic, $[11\bar{2}]$ azimuth;
(c) superimposed pattern; (d) hexagonal, $\langle 11\bar{2}0\rangle$ azimuth;
(e) cubic, $[1\bar{1}0]$ azimuth; and (f) cubic, $[1\bar{1}0]$ azimuth, twinned around [111] axis.

Reflection symbols:

● - hexagonal phase, △ - forbidden reflection for hexagonal phase,

□ - cubic phase, ○ - cubic phase (twinned position),

▣ - coincident reflections from hexagonal and cubic phase.

PL spectra assessed by the 325 nm monochromatic beam from a continuous wave He-Cd laser with a band pass filter. The luminescence spectra are obtained at room temperature, in which the relative intensities are plotted as a function of wavelength. From α-GaN epitaxial films grown on (0001) sapphire substrate, the intense peak of near-edge emission is shown at 372 nm (3.33 eV) and the relatively weak emission band due to its longitudinal optical phonon replica occurs around 390 nm (3.18 eV), as shown in Fig. 4a.

Neverthless, the mixed two-phase GaN epitaxial films grown on (0001) sapphire substrate give rise to two intense emission peaks, which are typically observed at 370 nm (3.35 eV) and 394 nm (3.15 eV), as shown in Fig. 4b. Obviously, the former is caused by (0001) GaN, but the latter seems to be intensified by (111) GaN. From the CL measurment by SEM at room temperature, the local CL spectra were separately derived from the surfaces of the island-shape (111) GaN and hexagonal-shape (0001) GaN, which show a strong broad singlet near 385 nm (3.22 eV) and a singlet near 364 nm (3.41 eV), respectively (Fig. 5). Indication is that the band gap energy of (111) GaN is smaller than the energy of (0001) GaN. The band gap value for β-GaN is estimated to be 3.18 ± 0.30 eV at room temperature.

3-4. About the mechanism of cubic phase formation on the (0001) surface of hexagonal phase GaN

The stable phase of gallium nitride is α-GaN with hcp wurtzite structure. The epitaxial films of gallium nitride on sapphire are of hexagonal structure under the steady-state growth conditions by means of the halide vapor phase deposition process. If the steady-state conditions are disturbed by the decrease in HCl-concentration as well as by the simultaneous lowering of the temperature, stacking faults are often produced on the (0001) α-GaN surface, followed by the growth of the cubic β-GaN oriented by (111) face parallel to (0001) face of α-GaN. It is interesting to note that the formation of cubic phase was observed only in (0001) films. According to Ref.[10], an explanation is attempted by the low value of △F (free energy change) of stacking fault formation on the (0001) face. Besides, the segregation of excessive metallic Ga may be formed due to the GaN dissociation at the growth temperatures, or uncontrolled impurities on the growing hexagonal surface may also favour the formation of the stacking faults. As seen from Fig. 1b, the cubic GaN islands have big sizes of more than 10 μm, i.e. GaN continues to grow even after the stoppage of the HCl flow into Ga-boat. Continuation of the GaN growth as cubic phase islands could be explained by

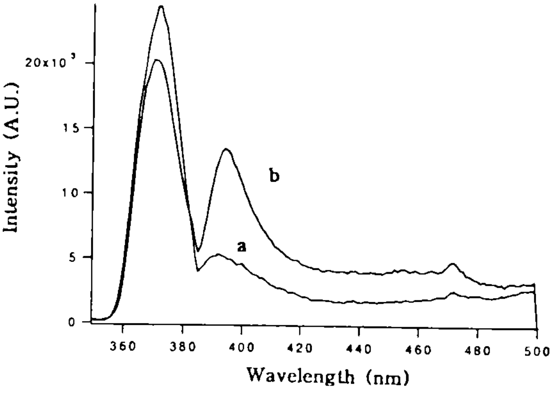


Fig. 4. PL spectra for (a) hexagonal phase GaN and (b) two-phase GaN.

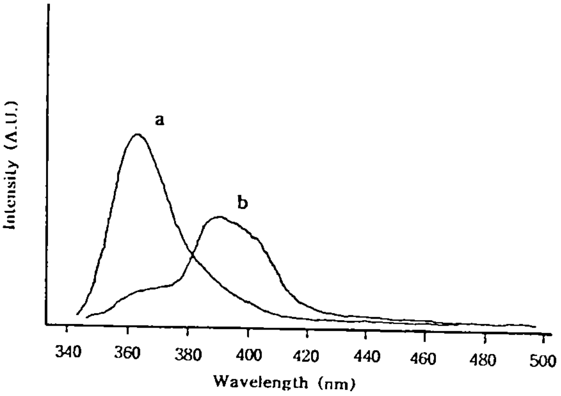


Fig. 5. CL spectra for (a) hexagonal phase GaN and (b) cubic phase GaN.

two possiblereasons; 1) due to slow diffusion of HCl from its feed line into Ga-boat, and 2) due to presense of uncontrolled impurities, such as H_2O vapor or oxygen, which is likely to be introduced into the gaseous phase. In the latter case metallic Ga can be transported to the substrates zone as the easily-volatile monoxide Ga_2O, which eventually interacts with NH_3 to form GaN.

4. Conclusions

The trigonally-shaped islands of β-GaN are formed on the (0001) surface of α-GaN under the unsteady-state growth conditions. The mutual orientation of cubic and hexagonal gallium nitride is: $[1\bar{1}0]$ (111)β-GaN//$[11\bar{2}0]$ (0001) α-GaN. The islands are twinned around [111]-axis. The initial stage of β-GaN growth is the formation of stacking faults in α-GaN due to disturbance of steady-state conditions on the surface.

Acknowledgments

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