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# Excitonic Emissions in GaN Films on AlN Substrates Using Microwave-Excited N Plasma Epitaxial Growth

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Gallium Nitride (GaN) films with hexagonal structure are grown on aluminum nitride substrates in gallium and nitrogen plasma exited by microwave power. The photoluminescence properties of GaN have been investigated at various temperatures. Only one peak at 3.477 eV arises in the whole spectral region at 4.2 K. The emission is considered to be $I_2$ line which is attributed to recombination of an exciton bound to a N vacancy.

## 1. Introduction

Gallium Nitride (GaN) shows great promise for LED and LD in the blue and ultraviolet (UV) region because of its direct and wide bandgap (Eg=3.39 eV at 300 K)[1]. GaN films have usually been grown by metal organic chemical vapor deposition (MOCVD)[2,3] or molecular beam epitaxy (MBE)[3]. However, MOCVD gives rise to contamination with carbon of starting material into GaN, and consequently the contaminant hinders the properties of GaN epilayers. On the other hand, MBE is necessary for growth under ultra-high vacuum which makes the usage difficult.

Since no bulk GaN single crystal is available for substrates yet, most of researchers have used sapphire, which causes a 14 % lattice mismatch to GaN. In many cases, aluminum nitride (AlN) has been grown on the sapphire substrate as a buffer layer to relax the lattice mismatch. It has been well-known that the AlN buffer layer improves effectively the structural properties of GaN[4].

In this paper, we will propose a new method for epitaxial growth of GaN. The method is based on reactions between active species of nitrogen and gallium excited in the plasma. We refer to this method as microwave plasma chemical vapor deposition (MPCVD). Using only high-pure Ga and $N_2$ gas as the starting materials, MPCVD can prevent impurities from incorporating into the GaN lattice. AlN ceramics with high quality were used as a substrate in this study.

## 2. Experimental

The GaN films were grown on AlN (Tokuyama Co. Ltd.)[5] in nitrogen-plasma produced by microwave power source (2.45 GHz). Figure 1 shows schematically the apparatus. Optical emission from the plasma was monitored with a monochromator to investigate plasma species related with formation of GaN. High-pure Ga (99.9999%) was used as the Ga source, and put in the plasma together with the substrate as shown in Fig. 1 (a). The growth zone was made of a quartz tube. The growth conditions were $N_2$ pressure of 4 Torr, $N_2$ flow rate of 500 ml/min, and microwave power of 500 W.

Crystal structure and quality were evaluated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Photoluminescence was excited with a He-Cd laser (325 nm) and a pulsed nitrogen gas laser (377.1 nm, a pulse width of 1 ns) between 4.2 and 300 K.

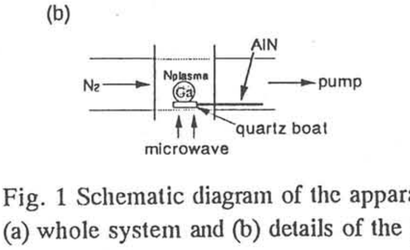


Fig. 1 Schematic diagram of the apparatus. (a) whole system and (b) details of the growth zone.

## 3. Results and Discussion

We measured emission from the plasma during growth.

Emission spectra were composed of peaks of the first positive and second positive series transitions of the natural $N_2$ molecule[6], the first negative series of the molecular $N_2^+$ ion[6] and atomic N[7] when the microwave power was lower than 500 W. In the region of higher microwave power, the intensity of atomic N peaks increased and two strong peaks newly appeared at 417 and 403 nm, respectively. The peaks are identical to atomic Ga[8]. When the peaks of atomic Ga were detected, GaN crystals can be grown on the substrates.

Figure 2 shows an x-ray diffraction pattern for the resulting material grown on AlN. The pattern shows mixed phases of hexagonal GaN and hexagonal AlN. However, the intensity of the (0002) peak is much larger than that theoretically expected. The GaN might be oriented to the hexagonal phase. A SEM picture reveals the granular nature and these grains are a few $\mu$m in diameter.

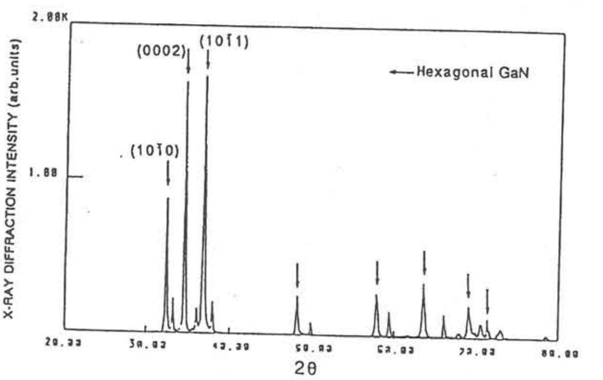


Fig. 2 X-ray diffraction pattern for GaN grown on AlN. The peaks denoted by arrows correspond to hexagonal GaN, and the others to hexagonal AlN.

Figure 3 (a) shows photoluminescence spectrum at 4.2 K of a GaN film grown on AlN by MPCVD. In the near-gap region, there exists a strong emission with a half-width of 89 nm (i.e. 0.088 eV) at 356.3 nm (i.e. 3.477 eV). The spectra exhibited no phonon replicas. This emission is therefore ascribed to the recombination of an exciton bound to a neutral donor ($I_2$ line). The binding energy of the exciton to the donor is estimated to be 6 meV if the free exciton emission occurs at 3.483 eV[9]. The result is in good agreement with that for $I_2$ line in other works[10, 11]. Taking account of undoped sample, an intrinsic N vacancy is the most possible candidate for the donor of the $I_2$ line.

It should be noted that emission from deep levels was absent in the present MOCVD-grown sample although GaN grown by MOCVD shows the emission band (so-called, Cband)[10] associated with carbon from starting materials. This means that the sample involves very few impurities because MPCVD uses only high-pure $N_2$ and Ga without organic matter.

As the temperature increased, the peak locating near band gap shifted to the lower energy side. Figures 3 (b) and (c) show the photoluminescence spectra at 77 and 300 K, respectively.

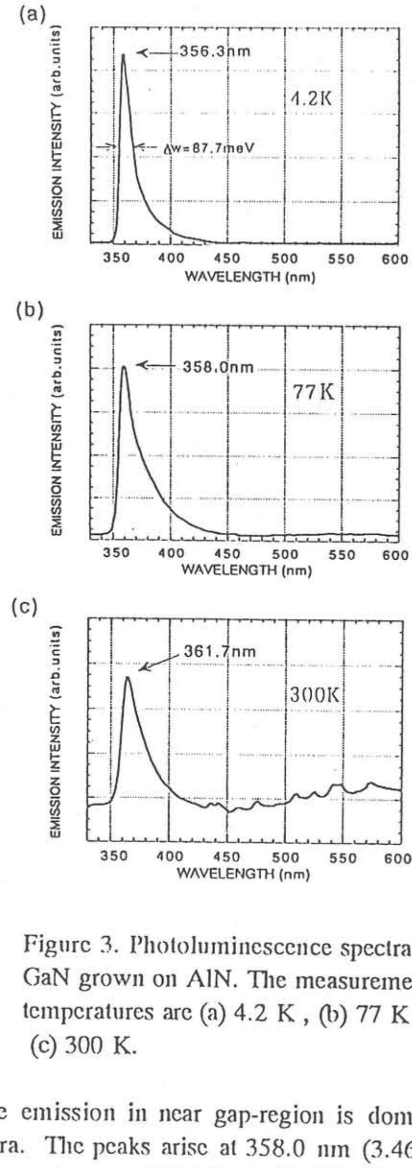


Figure 3. Photoluminescence spectra of GaN grown on AlN. The measurement temperatures are (a) 4.2 K , (b) 77 K and (c) 300 K.

The emission in near gap-region is dominant in both spectra. The peaks arise at 358.0 nm (3.461 eV) for the 77 K spectrum and 361.7 nm (3.425 eV) for the 300 K. Compared with the band gap of 3.470 eV at 77 K calculated by the expression $Eg=3.503+(5.08\times10^{-4}\times T^2)/(T-992)$[10], the emission at 77K is probably related to the $I_2$ line. However, since the tail to the side of longer wavelength becomes wider than that at 4.2 K, another emission seems to overlap with the $I_2$ line.

The strong emission at room temperature (RT) is remarkable for application to optical devices. Since the exciton should be dissociated at elevated temperatures, the $I_2$ line seems to be no longer responsible for the RT emission. It is probably due to band-to-band transition.

Time resolved luminescence spectra to characterize the near-band-gap emission at 77 K were measured. As shown in Fig. 4, the peak position is constant to variation of the delay time from 0 $\mu s$ to 25 $\mu s$. This leads no contribution of recombination of a donor-acceptor pair to the emission. The peak intensity decreased abruptly within 5 $\mu s$ and then gradually. The emission is likely composed of two components, the fast one of which corresponds to the $I_2$ line with a short life time.

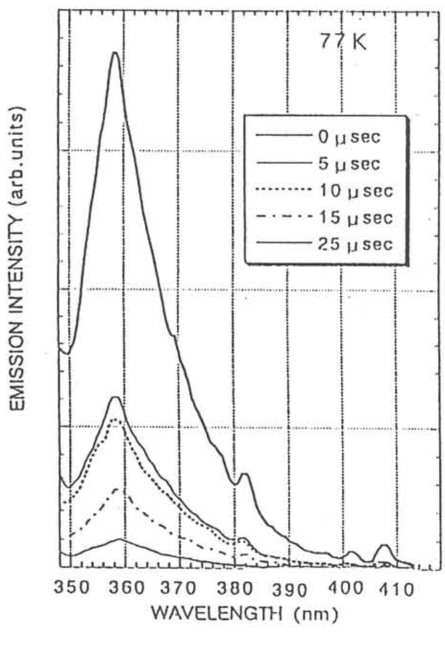


Figure 4. Time resolved luminescence spectra (77 K) of a GaN grown on a AlN substrate using MPCVD.

## 4. Conclusion

GaN with hexagonal structure was grown on AlN in $N_2$ and Ga plasma produced by microwave discharge. Although the resulting GaN film consisted of microcrystals, it showed a strong emission at 3.477 eV and no emission related with impurities at 4.2 K. The strong emission can be interpreted by $I_2$ line which is the recombination of an exciton bound to a N vacancy. Neither phonon replicas nor donor-acceptor emission were detected in the grown films. At 77 K, near- gap emission seems to consist of two components. One is the $I_2$ line with fast life time, and another is now unknown.

We can observe a strong emission probably due to band-to-band transition at 3.425 eV at room temperature. It is an important factor for application to UV optical devices. These results revealed that MPCVD method and AlN substrates are effective for epitaxial growth of GaN layers.

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