Metalorganic vapor phase epitaxial growth of a high quality GaN film using an AlN buffer layer

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Metalorganic vapor phase epitaxial growth of a high quality GaN film using an AlN buffer layer

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Atmospheric pressure metalorganic vapor phase epitaxial growth and characterization of high quality GaN on sapphire (0001) substrates are reported. Using AlN buffer layers, GaN thin films with optically flat surfaces free from cracks are successfully grown. The narrowest x-ray rocking curve from the (0006) plane is 2.70′ and from the (20$\bar{2}$4) plane is 1.86′. Photoluminescence spectra show strong near band edge emission. The growth condition dependence of crystalline quality is also studied.

GaN is one of the most promising materials for light-emitting devices in the spectral region of blue, violet, and ultraviolet, because it has a direct energy band gap of 3.39 eV.[1] For device fabrication, single crystals of smooth specular surfaces are required. Single crystalline GaN is usually grown on (0001) sapphire substrates.[2] However, it is fairly difficult to grow an epitaxial film of high quality with a smooth surface free from cracks, because of the large lattice mismatch (~13.8%) and the large difference of thermal expansion coefficient between the grown film and the substrate.[1,3] Yoshida *et al.* reported,[4] for the growth of GaN films by molecular beam epitaxy (MBE), the effectiveness of an AlN buffer layer between the grown film and the sapphire substrate for improvement of the electrical and luminescence properties. However, no investigations of the crystallinity and morphology were described. Furthermore, it has been reported that the electrical properties of GaN grown by MBE under high vacuum conditions are inferior to those grown by hydride vapor phase epitaxy (HVPE) at atmospheric pressure and by metalorganic vapor phase epitaxy (MOVPE).[4-6] This is possibly caused by the very high equilibrium pressure of nitrogen over GaN at typical growth temperatures, resulting in a high density of nitrogen vacancies. On the other hand, MOVPE has proven its suitability for the epitaxial growth of GaN of good quality.[6,7]

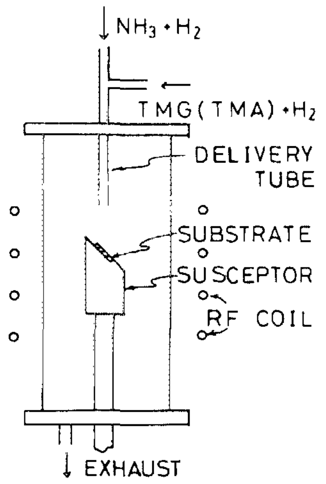

FIG. 1. Schematic drawing of the reactor part of the MOVPE system.

We report that, by using a thin AlN layer as the buffer layer, GaN single crystal films with optically flat surfaces free from cracks have been successfully grown by MOVPE for the first time. Investigations by double crystal x-ray diffractometry show that the crystalline quality of these films is much superior to those obtained to date. Surface morphology and luminescence properties of these films in relation to the growth conditions are also studied.

A conventional MOVPE system with a simple vertical reactor operated at atmospheric pressure was used. It is similar to that reported formerly.[7] In order to reduce undesirable reactions between metalorganic compounds and gaseous NH_3, and to improve the uniformity of grown GaN films, some improvements have been made in the reactor design and growth conditions as shown in Fig. 1. Metalorganic sources diluted with H_2 and a large amount of NH_3 with H_2 as a carrier gas were mixed just before the reactor and were fed through a delivery tube to a slanted substrate with a high velocity (~425 cm/s). Under these conditions, the aim has been successfully achieved. The substrates used were (0001) sapphire with a dimension of about 7×7 mm. Prior to growth, they were etched in a hot solution of 3:1 H_2SO_4:H_3PO_4 for about 12 min, and were heated to about 1150 °C in a H_2 stream for 10 min in order to remove surface damage.[8] At first, by feeding trimethylaluminum (TMA) and NH_3 gases into the reactor, a thin AlN layer was deposited. The substrate was then heated to a higher temperature at which GaN was grown by replacing TMA by trimethylgallium (TMG). The growth conditions are summarized in Table I. The thickness of the GaN films obtained under these

TABLE I. Growth conditions.

	AlN buffer layer	GaN film
Flow rate (cc/min) of		
TMG (at −15 °C)		10
TMA (at 15 °C)	20	
H_2 (diluent)	1000	1000
NH_3	2000	1500
H_2 (carrier gas)	3000	2500
Growth temp. (°C)	900–1000	950–1060
Growth time (min)	1	30

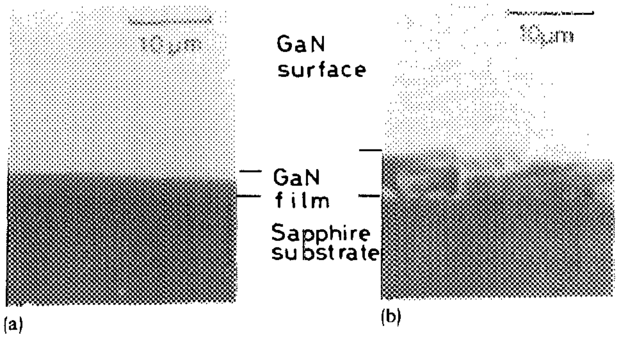

FIG. 2. SEM image of GaN film (a) with and (b) without the AlN buffer layer. No cracks are observed in the former. Bar indicates 10 μm.

conditions was in the range of 3.5–4.5 μm. The quality of the GaN films was strongly affected by the thickness of the AlN layer. For AlN deposition times exceeding 1 min, GaN films had a tendency to become polycrystalline. When the deposition temperature of AlN was fairly low (e.g., 800 °C), many pits appeared in the GaN film,[9] while above 1100 °C, hexagonal grains were observed. AlN layers deposited under conditions shown in the table were found to be amorphous, resulting in smooth, specular films of GaN.

Figure 2 shows scanning electron micrographs of GaN films grown with and without the AlN buffer layers. It is clearly seen that the former [Fig. 2(a)] has an optically flat surface and its thickness is quite uniform, while the latter [Fig. 2(b)] is not at all flat. In single crystalline GaN films grown by HVPE (and ordinary MOVPE), many cracks (⟨11$\bar{2}$0⟩ oriented) were observed.[10] This has been attributed to mismatches mentioned above. By using AlN buffer layers, cracks were much reduced in all samples and disappeared in samples grown below 1020 °C. Kikuchi lines were distinctly seen in reflection high-energy electron diffraction pattern of the GaN film grown with an AlN buffer layer, showing the good crystallinity and flatness of the film.

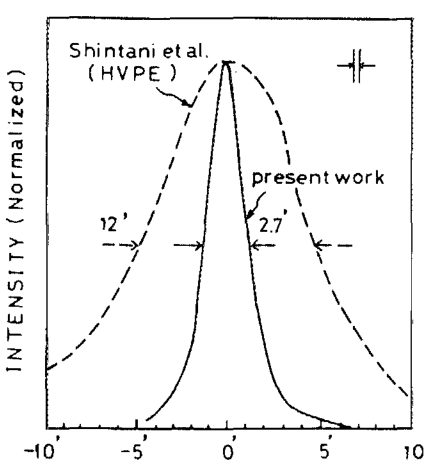

FIG. 3. X-ray rocking curve for (0006) diffraction from GaN grown at 970 °C with the AlN buffer layer. Dotted line shows data obtained by HVPE.[11]

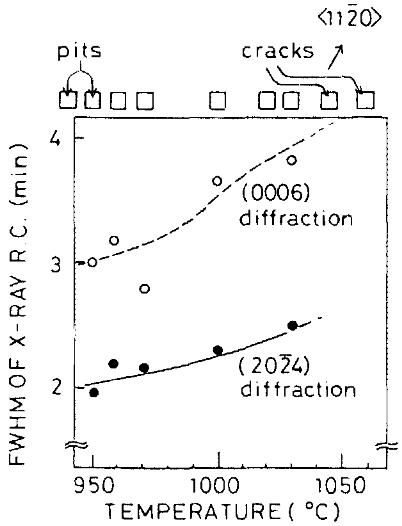

FIG. 4. Variation of FWHM of XRC (average of two different positions in the same film) and the appearance of the GaN film with the growth temperature. ⟨11$\bar{2}$0⟩ cracks are seen at higher temperatures and pits at lower temperatures.

Films were examined by double crystal x-ray diffraction, because the full width at half-maximum (FWHM) of the x-ray rocking curve (XRC) is a good measure of crystallinity. The XRC from (0006) diffraction of GaN grown at 970 °C is shown in Fig. 3, together with that of HVPE.[11] The narrowest FWHM obtained in this work is 2.70 min from the (0006) diffraction and 1.86 min from the (20$\bar{2}$4) diffraction. Such narrow FWHM's have never been reported in GaN. This indicates that the crystallinity of the GaN films grown with the AlN layer is fairly high. Figure 4 is the change of the XRC FWHM with the GaN growth temperature. The FWHM increases as the growth temperature is raised. This is probably caused mainly by the increases of the crack density as shown in the same figure. Below 940 °C, many pits appeared.

Photoluminescence (PL) spectra of GaN grown in this way showed very strong near band edge emission peaking at 3.360 eV (RT) and 3.474 eV (77 K). The yellow emission, which is thought to originate in impurities such as carbon or some impurity-defect complex,[12] was much weaker than that reported to date. The PL data suggest that the density of deep level impurities is fairly low.

In summary, the quality of GaN thin films grown by MOVPE using AlN buffer layers is shown to be excellent in terms of morphological, crystalline, and optical properties. The key growth parameters necessary to obtain high quality films are the thickness and the deposition temperature of the AlN buffer layer as well as the growth temperature of the GaN. Cracking of the GaN film and the substrate can be prevented effectively by the low-temperature growth of the GaN film using the AlN buffer layer.

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