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Analysis of polycrystalline GaN grown on a glass substrate

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Abstract

Polycrystalline gallium nitride layers were deposited by molecular beam epitaxy assisted by an electron cyclotron source or with an ammonia source. The deposition was carried out at 730, 810 and 850 °C. In the case of the ammonia source a low-temperature buffer layer was needed. The microstructure was analysed by transmission electron microscopy and the optical properties by means of photoluminescence (PL). With the ammonia source, the size of the grains was larger than with the electron cyclotron source and the PL intensity was more important. Correlations between the microstructure of the layers and the PL emission are proposed.

1. Introduction

III–V nitride semiconductors (GaN, AlN, InN) and their alloys are characterized by a direct band gap in the range of 1.8–6.2 eV making them excellent candidates for a large range of optoelectronic applications. These possibilities have led to the commercialization of devices emitting from amber to ultraviolet: light-emitting diodes and pulsed or continuous lasers. Layers of these nitrides grown on various substrates, mainly on sapphire and silicon carbide, contain a very high density of defects, threading dislocations, stacking faults and inversion domain boundaries [1]. Improvements have been obtained by using buffer layers or epitaxial lateral overgrowth with a density of threading dislocations as low as 10^5 cm^{-2} [2]. Another approach consists in making low-cost devices by using polycrystalline materials. Different substrates were used such as quartz glass, metal, silicon and ferroelectric and magnetic oxides [3–5]. Recently, light-emitting diodes were made from polycrystalline GaN grown on a quartz glass substrate [6]. Although the microstructure is polycrystalline, strong photoluminescence (PL) emission is observed without deep-level emission [7].

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In this study, we have performed PL analysis and transmission electron microscopy (TEM) observations in order to determine the possible correlations between the microstructural characteristics and the PL emission.

2. Experiments

Two types of specimen were grown either in an ammonia source molecular beam epitaxy (NH₃-MBE) system or by MBE assisted with electron cyclotron resonance (ECR-MBE). The substrates used were quartz glass. In the first case, NH₃-MBE, after thermal cleaning at 900 °C for 10 min a low-temperature buffer layer was grown at 550 °C; this was followed by deposition of the GaN layer at 850 °C with an ammonia flow rate of 50 sccm and a gallium flux of 2.0×10^{-7} Torr. The growth rate was approximately $0.5 \mu\text{m h}^{-1}$ and the thickness of the layer was $1.0 \mu\text{m}$. For the ECR-MBE experiments, the conditions were slightly different. Elemental gallium and ECR plasma-enhanced nitrogen were used as group III and group V sources, respectively. The substrate surface was sequentially cleaned in hot baths of trichloroethylene, acetone and alcohol. Additional etching was not conducted. After loading in the growth chamber, thermal cleaning was carried out at 800 °C for 10 min and for 3 min under plasma-enhanced nitrogen irradiation just before growth was induced. The layers were grown at 730 °C (specimen G) and at 810 °C (specimen A) to obtain a final thickness in the 0.2–0.4 μm range. The growth rate was approximately $0.2 \mu\text{m h}^{-1}$ with nitrogen flow rates of 1.5 sccm (specimen G), 1.0 sccm (specimen A) and gallium fluxes of 2.35×10^{-7} Torr (specimen G), 3.95×10^{-7} Torr (specimen A). PL measurements were conducted using a He–Cd laser (325 nm, 27 mW) as an excitation light source.

TEM observations were carried out with a JEOL 2010 TEM operating at 200 keV. After the specimens had been ground down to 100 μm thickness, they were dimpled to 10 μm and finally ion thinned with 5 keV argon ions to electron transparency.

3. Results and discussion

3.1. Structural analysis

NH₃-MBE growth needs a buffer layer to initiate the development of the GaN layer. At 550 °C the layer is amorphous, as shown by reflection high-energy electron diffraction (RHEED). After heating up to 850 °C, rings in the RHEED patterns form due to the crystallization of the deposited material. Their intensities are uniform and no preferential orientation is observed. Then, the layer grows with a preferential orientation nearly parallel to the *c*-axis, as shown by x-ray diffraction, and the mean grain size is 500 nm, deduced from atomic force microscope measurement on the top surface [8]. An electron micrograph confirms the polycrystalline microstructure of the layer with grains containing defects which are mainly basal stacking faults (figure 1). They are more or less parallel to the plane of the interface with the substrate, in agreement with the *c*-orientation of the layer. A few planar defects parallel to the growth direction are also visible within some grains; they may be attributed to stacking faults of the other type, which are in the prismatic planes. Their atomic structure was previously analysed and most of them were described by considering the Drum model [9]. At the level of the interface, no reaction with the substrate is detected, but some holes, black areas in figures 1 and 2, are present. They form at the interface and could be due to a non-perfect coverage of the substrate during the deposition of the buffer layer which is necessary to grow the layer when ammonia is used. However, it is worth noting that grains contain no threading dislocations, unlike the GaN layers with a mosaic microstructure exhibiting a dislocation

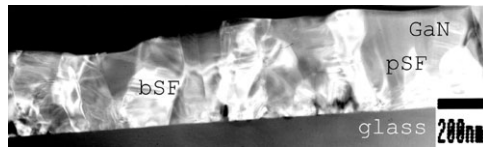


Figure 1. Polycrystalline structure of the NH_3 -MBE specimen; bSF, pSF: basal and prismatic stacking faults.

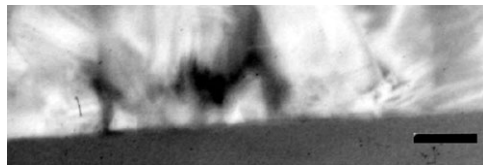


Figure 2. A NH_3 -MBE specimen: formation of holes at the interface with the substrate (marker: 50 nm).



Figure 3. A NH_3 -MBE specimen: a GaN layer showing a rough top surface (thickness: 500 nm).

density as high as 10^{10} cm^{-2} . Although no systematic contrast analysis is presented, the absence of any dislocations is verified in figure 3 for a grain crossing the whole layer. It is also possible to observe the strong roughness of the top surface. The plan view shows the excellent quality of the grains, 200 nm in mean diameter, with misorientations in the 1° – 20° range about the c -axis and grain boundaries which are well faceted along the $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ prismatic planes (figure 4).

For the ECR-MBE specimens, two conditions of growth have been chosen: specimen A at 810°C and specimen G at 730°C ; ratio Ga/N_2 ($10^{-7} \text{ Torr sccm}^{-1}$) = 3.95/1.0 and 2.35/1.5, respectively [10]. The microstructure of specimen A is characterized by a columnar growth with a mean diameter of 50 nm. The growth direction is nearly parallel to the c -axis; the deviation between adjacent grains deduced from the electron diffraction pattern is about 10°

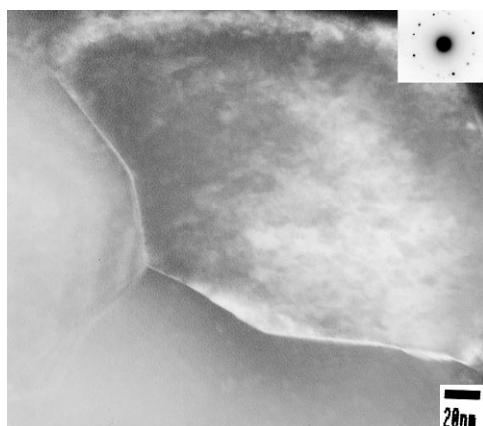


Figure 4. A NH_3 -MBE specimen: faceting of the grain boundaries (a plan view along [0001] axis).

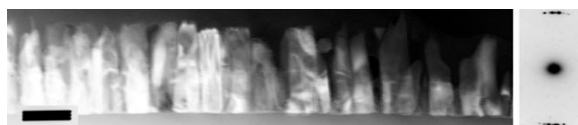


Figure 5. Specimen A, ECR-MBE at 810 °C, columnar growth (marker: 100 nm), with the electron diffraction pattern; g : 0002, showing a maximum deviation of 10° from the normal to the interface.

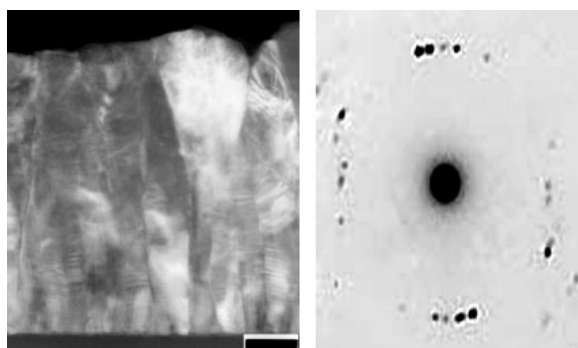


Figure 6. Specimen G, ECR-MBE at 730 °C, columnar growth with a deviation of 20° for the c -axis (marker 50 nm); g : 0002, with respect to the substrate normal.

with an upper limit of 20°. The grains contain basal stacking faults as major defects. The roughness of the top surface seems to be less important (figure 5).

The second specimen, G, has been prepared at a lower temperature, 710 °C, and for a lower GaN/N₂ ratio than the first one, specimen A. Lowering the growth temperature results in reduced re-evaporation of N atoms from the surface and produces a similar condition to a N₂-rich condition. Therefore, these conditions reduce the surface migration of gallium atoms. The mean diameter is about 30 nm (figure 6) and the deviation of the growth direction is more important: 20° is the mean value rather than the 10° for specimen A grown at 810 °C.

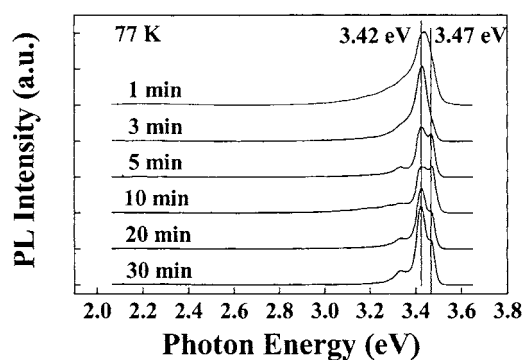


Figure 7. 77 K PL spectra for the NH_3 -MBE specimen as a function of the buffer layer growth time.

3.2. Photoluminescence spectral analysis

PL emission is very sensitive to the crystalline quality of the layers. The larger and more uniformly oriented the grains are, the stronger and narrower the PL emission is [11]. For NH_3 -MBE growth, at room temperature the peak energy is at 3.406, 3.423 eV for MOVPE growth, the full width at half-maximum (FWHM) is as broad as 89.4, 66 meV for MOVPE growth, but the PL peak intensity was slightly stronger than for MOVPE-grown single-crystal GaN. Moreover, the integrated PL intensity is much stronger and exceeds that of single crystal. This strong emission of polycrystalline GaN on a quartz substrate was also demonstrated previously [12]. This result was obtained after optimization of the growth conditions of the buffer layer; it was demonstrated that the 10 min LT buffer layer growth was the best condition with dominant peaks at 3.42 and 3.47 eV, 77 K (figure 7) [8]. The emission peak at 3.42 eV was previously attributed to a defect-related transition [10]. It is known that basal stacking faults can induce excitonic transitions around 3.41–3.42 eV [13]. The high density of these defects favours this interpretation.

For ECR-MBE, the PL spectra at 77 K show some differences. Specimen A presents the same characteristics as a single crystal grown on a sapphire substrate. The position of the major peak is the same, 3.48 eV, and the FWHM is almost the same, 30 meV. By varying the temperature, the activation energy is deduced and found equal to 24 meV, which is in agreement with the activation energy of free excitons. The variation of the PL peak position can be fitted with the temperature dependence of the band gap energy. The difference between growth on sapphire and on a glass substrate may be explained by considering the origin of the strain for both substrates. A GaN layer grown on a sapphire substrate leads to compressive strain during the cooling from the growth temperature. It results in a shift of the exciton energy toward higher energy. On a quartz substrate the opposite situation is expected; the GaN layer is under tensile strain and there is a shift to lower energy. It was shown that the grain boundaries induce a compressive strain. Therefore, in a polycrystalline layer the tensile strain is equilibrated and even cancelled by the grain boundaries [10]. The other sample, specimen G, presents a red-shifted peak position, 3.43 eV, and a broader FWHM, 161.1 meV. However, the intensities are comparable. In this case, the shift due to the strain is not compatible with the previous fit of the variation of the PL peak energy with increasing strain suggested by considering a free exciton mechanism and another origin must be proposed. One possibility is that the 3.43 eV PL peak is linked to excitons bound to structural defects such as the basal stacking faults. However, the effect of the polycrystalline nature of the GaN layer was previously

observed [14]. By comparison with a sapphire substrate, it was concluded that the unique difference was a lower-energy band tail for the quartz substrate.

4. Conclusions

The band structure of materials is strongly affected by structural defects. In these polycrystalline GaN layers the main defects are the grain boundaries. These grain boundaries may be described as low-angle or high-grain boundaries according to the misorientation angle, the limit being considered as about 15° due to the possible overlapping of the cores. Whatever their crystallographic descriptions, they contain dislocations which are crystal dislocations regularly spaced for the low-angle grain boundaries. In the case of high-angle grain boundaries, they may be described as general or special if they correspond to specific misorientations within the concepts of the coincidence site lattice description [1]. These dislocations may introduce levels in the band gap for semiconductors or be the origin of the band tailing. In the polycrystalline layers analysed the microstructure, grain size and direction of growth vary. Even if dislocations are not shown, they are present in the grain boundaries and their density is proportional to the grain size. So, the associated disorder at the origin of the band tailing should modify the parameters of the PL spectra. The PL emission for the ECR-MBE layers is in agreement with the characteristics of the microstructure: the specimen A grain size is larger than that of specimen G and the deviation of the growth direction with respect to the substrate normal is less important. Another feature of these layers is the high density of basal stacking faults which could contribute to the formation of the peak at 3.42 eV.

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