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Ammonothermal growth of GaN crystals on HVPE-GaN seeds prepared with the use of ammonothermal substrates

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ABSTRACT

Results of gallium nitride crystallization by ammonothermal method are presented. GaN crystals grown earlier by a HVPE method on an ammonothermal GaN substrate and an MOCVD-GaN/sapphire template were used as seeds. Structural and optical properties of the obtained materials are studied and compared. Large radius of curvature (>100 m) and low dislocation density (7×10^4 cm^{-2}) can be reproduced in the ammonothermal method using an HVPE-GaN seed grown before on ammonothermal GaN. This proves that the use of HVPE-GaN grown on ammonothermal seeds allows to reproduce high crystallinity in a subsequent ammonothermal growth. It also demonstrates that a much more effective multiplication process of high quality GaN can be launched using a combination of the ammonothermal and HVPE methods.

1. Introduction

It has been shown that GaN growth from solution in supercritical ammonia (the ammonothermal method) in basic environment can result in crystals of exceptional structural quality (low dislocation density and flat crystallographic planes) [1]. The ammonothermal method is regarded as an analog of the hydrothermal method, commonly used in industrial production of quartz. The main difference is the use of supercritical ammonia instead of supercritical water. In the ammonothermal method, feedstock material (GaN) is dissolved in supercritical ammonia and transported by convection to a crystallization zone, where native seeds are placed. In this zone the solution is supersaturated and the crystal growth takes place. Some mineralizers are added to ammonia and their kind, basic or acidic, divides the ammonothermal method into ammonobasic [1–6] and ammonoacidic [7–9]. In the case of the basic ammonothermal growth, the temperature of the feedstock is lower than the temperature of the seeds, but solubility of GaN in ammonia is much higher at lower temperature. This means that the growth process is carried out in a retrograde solubility mode. The ammonothermal method enables the growth of crystals of large diameters (exceeding 2 in.) and high crystalline quality. It is a well-controlled and reproducible process performed at a relatively low temperature ($\sim$400 °C). Although the growth rate in ammonobasic conditions is quite low (maximum value reported today is 344 μm/day in the *c* direction [3]), this method enables growth of many crystals in one run at minimal material cost.

On the other hand, due to a high growth rate (>100 μm/h) hydride vapor phase epitaxy (HVPE) is the most popular method for production of GaN crystals, substrates, and wafers [10]. In the HVPE technology, GaN crystals are grown on foreign substrates, mainly MOCVD-GaN/sapphire templates or gallium arsenide (GaAs) wafers. The new-grown crystals are separated from the foreign MOCVD templates by a self-lift-off procedure and from the GaAs seeds by etching. Due to lattice and thermal mismatches between the new-grown material and the foreign seeds, threading dislocation density (TDD) in HVPE-GaN crystals is generally higher than 10^6 cm^{-2} and their (00.1) crystallographic planes are strongly bowed (radius of curvature <10 m).

It was shown that ammonothermally grown GaN (Am-GaN) crystals can be successfully used as seeds in the HVPE technology [11,12]. Crack-free HVPE-GaN layers of thickness up to 2 mm were deposited. They were grown with rates varying from 120 to 240 μm/h. Free-standing HVPE-GaN crystals can be obtained by slicing the layers from the Am-GaN seeds. The HVPE material reproduces the structural properties of the Am-GaN seed. An average dislocation density is of the order of 5×10^4 cm^{-2}, full

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width at half-maximum (FWHM) of the X-ray rocking curve (RC) for the (002) reflection is 20 arc s [13]. These results strongly suggest that it is feasible to multiply ammonothermal GaN crystals using the HVPE method. However, it has not yet been demonstrated that using HVPE-GaN as a seed allows to crystallize ammonothermal GaN of high structural quality. Pure scientific curiosity lead to studying the synergy of ammonothermal and HVPE methods. This resulted in a proof of concept that multiplication of ammonothermal seeds and reproducibility of their outstanding structural quality using the HVPE method is possible. In this paper, results of ammonothermal growth on an HVPE-GaN crystal previously crystallized on an Am-GaN seed are shown and discussed. They are compared with results of ammonothermal growth on HVPE-GaN grown before on an MOCVD-GaN/sapphire template and on a native Am-GaN seed.

2. Experimental

Free-standing HVPE-GaN crystals were used as seeds for an ammonothermal growth run in basic environment. Three 1-in. and 300-μm-thick samples were applied: HVPE-GaN previously grown on an Am-GaN seed (HVPE-GaN(A)), HVPE-GaN grown before on an MOCVD-GaN/sapphire template (HVPE-GaN(S)), and a typical Am-GaN crystal grown previously on an Am-GaN seed as a reference sample. The growth process was carried out in the $-c$ direction. The $(00.\bar{1})$ surfaces of all seeds had not been treated by chemo-mechanical polishing before the crystallization run due to a back-etching phenomenon occurring at the beginning of an ammonothermal growth process. Therefore, preliminary mechanical polishing is sufficient to prepare the surface of the seed.

In order to avoid stress generation, it is necessary to match the free carrier concentration in the seed and overgrown Am-GaN crystal. A free electron concentration of the HVPE seeds was of the order of 3–5×10^{16} cm^{-3}. Therefore, growth conditions during the ammonothermal process were appropriately adjusted in order to obtain Am-GaN crystals with electron concentration of about 5×10^{17} cm^{-3}. The free carrier concentration is correlated with oxygen content in the material [14]. A reduction of the oxygen content to the level of 1×10^{18} cm^{-3} was achieved by introducing an appropriate getter into the growth environment. Since the lowest possible to achieve electron concentration in the ammonothermal method is 5×10^{17} cm^{-3}, this value seems to be the best possible match. The difference between electron and oxygen concentrations may result from a partial compensation by gallium vacancies-related defects (acting as acceptors), identified recently in Am-GaN crystals [15].

Ammonothermal crystals grown on three kinds of seeds were studied with the use of X-ray diffraction technique. A high-resolution Panalytical X'Pert Pro MRD with a Cu Kα1 line source of 1.540597 Å wavelength was used. It was equipped with a 4-reflection Ge(220) Bartels monochromator and slit (0.1 mm × 0.1 mm) for the incident beam and an open detector for the diffracted beam. This set-up was used for measurements of the radius of curvature by collecting (00.2) reflections in few collinear points separated by 2 mm. Additionally, rocking curves and reciprocal space maps (RSMs) of symmetrical (00.2) and asymmetrical (01.5) reflexes, together with the c lattice parameter were measured on $(00\bar{1})$ GaN surfaces using a triple-axis mode with a 3-bounce analyzer crystal before the detector. Thanks to large thicknesses of the samples (above 1 mm), measurements at M-faces and then the a lattice constant, using in-plane diffraction on the (10.0) plane were also performed. For these measurements, $(00.\bar{1})$ surfaces of the HVPE seeds were prepared with mechanical and chemo-mechanical polishing in order to remove a subsurface damage layer created by slicing, which may affect the results of structural investigations, while $(00.\bar{1})$ and (10.0) overgrown Am-GaN surfaces were as-grown. Defect selective etching (DSE) in molten KOH–NaOH eutectic with 10% MgO (E+M etch [16]) was performed on as-grown $(00.\bar{1})$ surfaces at temperature of 500 °C during 20 min in order to determine the etch pit density. Electron concentration in the examined crystals was estimated from the level of free carrier absorption in the near-infrared range, basing on a previously performed calibration with the Hall effect measurements.

For contactless electroreflectance (CER) measurements the samples were placed in a capacitor with a half-transparent top electrode made from a copper-wire mesh [17]. The distance between the sample surface and the top electrode was ~0.5 mm. A single grating 0.55 m focal-length monochromator and a photomultiplier were used to disperse and detect the light reflected from the samples. The photoluminescence (PL) measurements were performed by exciting the samples with a 266 nm line of a pulse laser. The PL signal was detected by a spectrometer with a Si CCD detector. The absorption coefficient was measured using a double beam UV–VIS-NIR Cary 5 spectrophotometer in the wavelength range 320–3000 nm.

3. Results and discussion

Fig. 1 presents a photograph of a 1-in. 1.5-mm-thick Am-GaN crystal grown on the HVPE-GaN(A) seed. This crystal was crack-free and transparent, with an absorption coefficient of about 3 cm^{-1} at a wavelength of 450 nm. The value of the electron concentration in Am-GaN was 5×10^{17} cm^{-3}. Similar results were obtained for Am-GaN grown on HVPE-GaN(S) and the reference Am-GaN seed. This shows that the conditions of the ammonothermal growth process were properly adjusted and the intended oxygen concentration was achieved.

Table 1 shows results of XRD measurements of the grown Am-GaN crystals and the seeds. The values of FWHMs for the crystal grown on the HVPE-GaN(A) seed were 20 arc s and 56.5 arc s for the symmetric (00.2) and asymmetric (01.5) reflection, respectively. For the Am-GaN crystal grown on the HVPE-GaN(S), values of FWHMs for the same reflections were 570 arc s and 280 arc s. In case of the reference crystal grown on the Am-GaN seed, FWHMs for both reflections were very narrow (20 arc s). The value of the radius of curvature was about 100 m for Am-GaN grown on HVPE-GaN(A), 0.7–0.8 m for the crystal grown on HVPE-GaN(S), and exceeding 100 m for the reference sample. Rocking curves measured for the three described above Am-GaN crystals are presented in Fig. 2. It should be noted, that it is impossible to improve the structural quality of the HVPE-GaN(S) by the ammonothermal growth. It seems that HVPE-GaN grown before on an MOCVD-GaN/sapphire template can often be plastically (instead of elastically) deformed and the regrowth procedure does not improve its poor structural quality. A similar phenomenon was also observed in case of HVPE or HNPS GaN regrowth processes [18,19]. The twofold increase of FWHM of (01.5) reflection for Am-GaN/HVPE-GaN (A), as compared to Am-GaN/Am-GaN, may come from its smaller

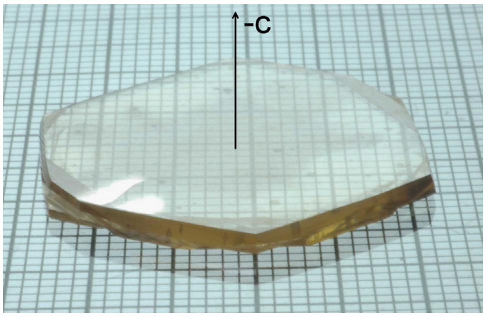

Fig. 1. Photograph of the 1-in. c-plane oriented ammonothermal crystal grown on the HVPE-GaN(A) seed.