Apporaches to Growth of GaN Substrates

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ABSTRACT

The successful growth of single crystal GaN substrates by HVPE on nearly lattice matched $LiGaO_2$ and $LiAlO_2$ substrates is reported. A critical step to obtaining high quality GaN films was initial surface nitridation. A spontaneous releasing technique was developed that leaves freestanding single crystal GaN without mechanical or chemical treatment. In addition, a process was developed to deposit GaN on Si (111) by a two-step low-temperature MOCVD step followed by a low-temperature HVPE growth in the same reactor. It was found that a SiO_x compliant interface was needed to relieve stress at the substrate-film interface. It was shown experimentally and theoretically that low-temperature growth prevented the formation of detrimental SiN_x. Surface morphology was observed by AFM; the structural quality was analyzed by XRD; the chemical composition was investigated by AES, ESCA and SIMS, and Raman spectroscopy was used to measure residual stresses.

Introduction

The III-nitride wide band-gap semiconductors show considerable potential for optoelectronics devices, as well as devices for use in extreme environments and high-power application [1-3]. Foremost among these materials is gallium nitride and its alloys with Al and In, with which blue and ultraviolet LEDs and lasers are produced.

Most commercial GaN-based devices rely on sapphire or occasionally SiC as the substrate. Unfortunately, the large lattice and thermal expansion mismatches between GaN and these substrates, result in high dislocation densities and residual stress, which deleteriously affect the optical and electrical performance of the fabricated devices [1, 4]. Epitaxially laterally overgrown (ELOG) GaN on sapphire has been used to reduce the number of threading dislocations in the GaN layer, and thus improve device performance and lifetimes, although issues remain with this approach. The ongoing effort to improve GaN film properties has driven the research community to seek alternative substrate materials. The obvious solution to minimizing defect generation at the interface is to use GaN substrates (9,10). At present, the most common approaches to growth of single crystal bulk substrates are high-pressure synthesis (8) and hydride vapor phase epitaxy (HVPE) of thick films on SiC or sapphire substrates with subsequent substrate removal by reactive ion etching, laser ablation, or polishing.

In this report, a summary of the results of investigations of nearly lattice matched $LiGaO_2$ and $LiAlO_2$ substrates as well as the more recent results with Si are presented (5-7).

EXPERIMENT

In addition to a conventional MOCVD system (Japan Oxygen) used for thin film growth of GaN, a novel technique for the deposition of GaN was used that could alternate between MOCVD and HVPE, combining the advantages of both. In the HVPE mode, trimethylgallium (TMG) is first reacted with HCl in the source zone of the hot wall reactor (Figure 1) to form chlorinated gallium species according to the following reaction:

$$Ga(CH_3)_3 + HCl \rightarrow GaCl + 3CH_4$$

Note that methyl radicals are easily converted to methane gas, so essentially that measured carbon incorporation is typical of MOCVD GaN. The stream is then combined with NH_3 in the downstream mixing zone and passed over a substrate where deposition of GaN occurs by the traditional HVPE reaction:

$$GaCl + NH_3 \rightarrow GaN + HCl + H_2$$

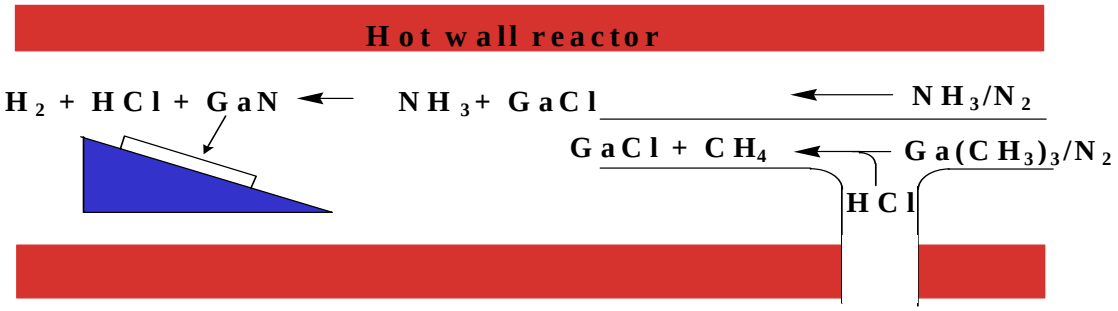

Figure 1. H-MOVPE reactor schematic.

Eliminating the HCl flow yields a hot-wall MOCVD growth process. The high flow rates and low source zone temperature prevent upstream decomposition of the TMG. The advantages of this technique include: MOCVD or HVPE in the same reactor, high growth rates, rapid reactant switching, lower background impurities with HCl (Cl retains metal impurities in the vapor phase), in-situ etching, elimination of HVPE source problems and finally improvement of NH_3 cracking.

Results and Discussion

$LiGaO_2$ Orthorhombic lithium gallate is a promising substrate for the growth of GaN films because of its close lattice mismatch (~1%) to GaN. It was determined that the use of a nitrogen carrier gas was essential to achieve high structural quality GaN on $LiGaO_2$. This was due to reduction of the substrate by H_2 as the carrier gas. Furthermore, the nitridation of $LiGaO_2$, using NH_3 prior to growth, improved the film quality. For the growth of thick GaN films it was a critical step in film-substrate self-separation that was observed upon cooling. Nitridation of the $LiGaO_2$ substrate leads to the reconstruction of the substrate surface and to the formation of a thin layer of nitrided material having the same orientation as the underlying substrate. For example, nitridation in NH_3 at 800 °C for 10 min yielded a smooth growth surface with an RMS roughness of 0.12 nm as measured by AFM. Examination of the nitrided surfaces with AES shows a distinct N_{KLL} peak on NH_3 pretreated surface, indicating that nitrogen was incorporated into the $LiGaO_2$ surface layer (8% estimated).

It is believed that the essential role of the nitridation step is to supply nucleation centers to promote the growth of GaN through a decrease in the interfacial free energy between the film and substrate. SIMS and ESCA analyses indicated that GaN forms on nitrided $LiGaO_2$ surface. Nitridation of the $LiGaO_2$ improves surface structure and surface reconstruction occurs as judged by HRTEM (11).

The nitrided layer also prevents the diffusion of Li into the GaN film (12). The quality of the GaN grown on the pretreated $LiGaO_2$ substrates was remarkably high. An estimated density of threading dislocations was only 10^7 cm^{-2} at a distance greater than 0.3 μm from the interface (Figure 2).

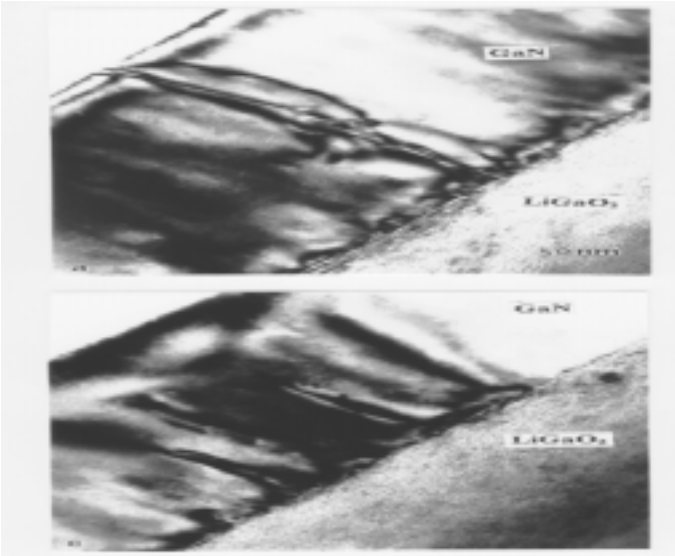

Fig. 2. XTEM micrographs of GaN grown on $LiGaO_2$, T = 850 °C.

Freestanding bulk GaN crystals with a maximum size of 10 x 10 x 0.3 mm^3 were obtained without any mechanical or chemical treatment. To obtain the self-separation, a seed GaN layer was first grown by MOVPE on (001) $LiGaO_2$ substrates to protect the substrate from the HCl attack. The substrate was then pre-heated in nitrogen, followed by a nitridation step using NH_3 (13,14). The GaN layers were grown on the nitrided surfaces at 850 °C and atmospheric pressure. A thick GaN layer was grown at 850 to 950 °C to a thickness in the range 100 to 300 μm. The last step was growth of a thin (0.1 to 0.2 μm) MOVPE GaN layer to improve the surface morphology of the growing film, presumably due to a change in surface polarization.

$LiAlO_2$ The tetragonal lithium aluminum oxide is similarly well lattice matched to GaN, but its chemical and thermal stability are superior to $LiGaO_2$. The lattice mismatch of –1.4% in the c-direction, and –0.1% in the b-direction, while larger than the <0.1% mismatch of $LiGaO_2$, this is still significantly better than the 16% lattice mismatch of GaN on c-plane sapphire.

Freestanding single crystalline GaN substrates were produced by spontaneous release of films grown on $LiAlO_2$ substrates using a similar process to that described above. The initial nitridation step was found to incorporate nitrogen into the $LiAlO_2$ substrate surface and to significantly decrease the surface roughness. While not as structurally perfect as films grown upon $LiGaO_2$, the GaN/ $LiAlO_2$ films were single-crystalline and possessed superior mechanical stability and background impurity concentrations.

Raman spectroscopy was used to investigate the variation of stress with the duration, and therefore thickness, of the initial MOCVD layer. Figure 3 demonstrated that the change in stress was small when comparing different $LiAlO_2$ samples, but large when compared

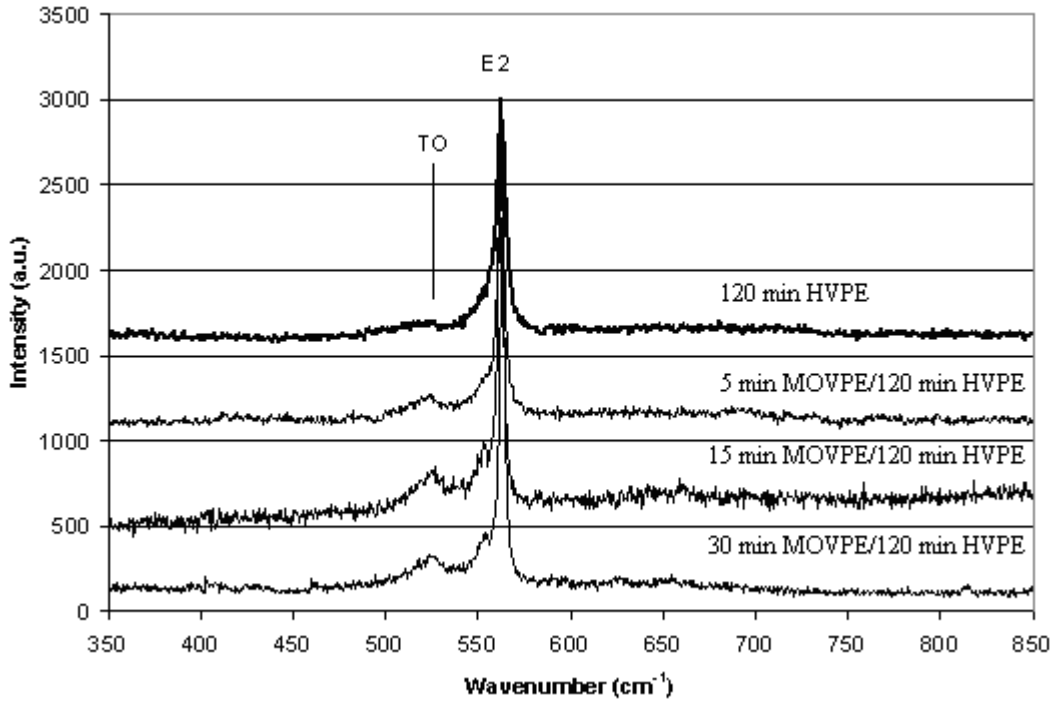

Figure 3. Raman spectra of freestanding GaN films grown upon LAO substrates with different initial MOVPE growth times.

to the films grown on nearly lattice-matched $LiGaO_2$. Because the Raman system was set up in Stokes mode, the E_2 shift due to compressive stress will decrease the wavenumber of stressed films. The stress-sensitive E_2 line was to a first approximation the same for each sample, located at 562 cm^{-1}, but was significantly shifted from the 566.2 cm^{-1} E_2 line of freestanding GaN grown by the high-temperature high-pressure technique. This indicated that, while the GaN/ $LiAlO_2$ films were nearly lattice-matched (though not as well as $LiGaO_2$), residual stress was both apparent and measurable (15). The in-plane strain $\epsilon_{||}$ was calculated to be +0.0031, and the stress was calculated to be 0.677 GPa.

Silicon Two of the main factors associated with substrate choice are cost and resulting GaN epilayer quality. A more recent research effort is on the use of Si substrates since it is relatively inexpensive, highest quality and large area, and presents many manufacturing advantages over other available substrates such as sapphire and SiC. The key disadvantage of Si as a substrate for GaN heteroepitaxy is the +20.5% misfit. In addition, the thermal expansion misfit between GaN and Si may lead to cracking in films grown at high temperature.

Initial attempts at GaN grown at high temperature (900 ^oC growth of a thin MOCVD protective layer followed by a thick HVPE layer) on a Si Substrate resulted in poly-crystalline GaN. Most likely an amorphous SiN_x layer formed at the Si/GaN interface, encouraging growth of GaN in its hexagonal modification with some cubic grains. Using low temperature MOCVD followed by high temperature HVPE resulted in cracking and peeling of the film caused by the large thermal mismatch between GaN and Si. Single crystal GaN was produced, however, using a low temperature MOCVD layer (560 ^oC)

followed by a low temperature HVPE GaN layer (560 ^{o}C). Figure 2 shows a cross-sectional SEM micrograph of the resulting structure.

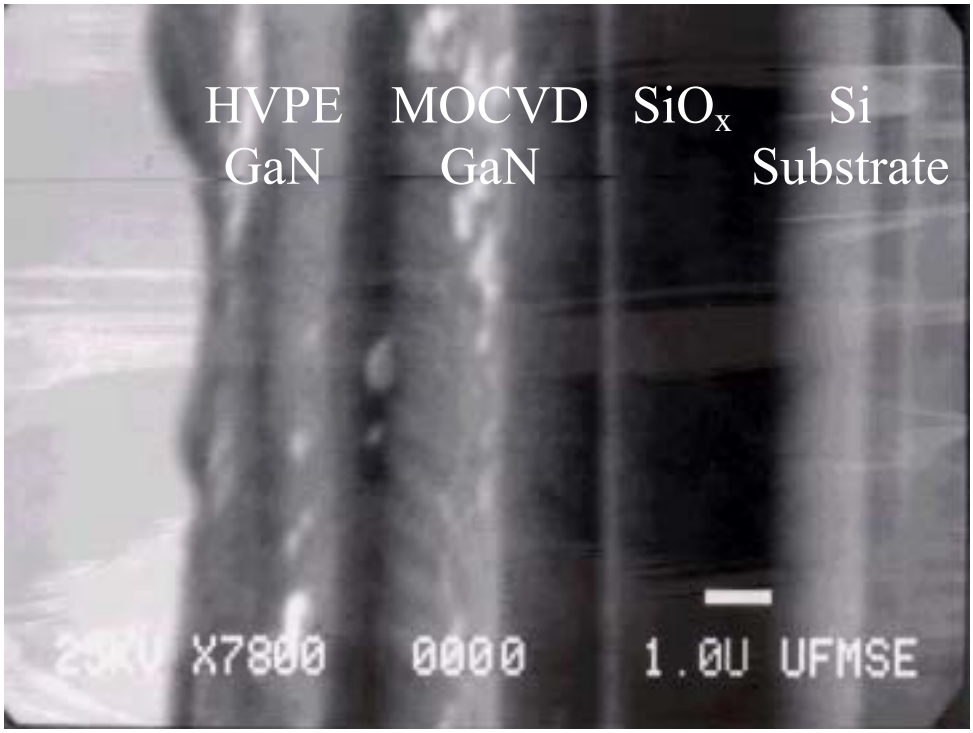

Figure 2. XSEM of low-temperature MOCVD/HVPE GaN.

A sharp interface between the MOCVD and the HVPE layers is evident. Also evident in this micrograph is the formation of a SiO_x layer between the GaN and Si. It is possible that the SiO_x layer acts as a compliant interface, reducing the stress between the GaN and the Si substrate. XPS and AES analysis of the near surface region of the GaN suggested there is no chlorine present. Additionally, the GaN surface was specular and smooth as judged by AFM. XTEM characterization shows that dislocations formed at the substrate/film interface and thread into the film. More importantly, a sharp selected area diffraction pattern provided confirmation that the GaN film is single-crystal.

CONCLUSIONS

Freestanding GaN substrates were grown by HVPE on nearly lattice-matched $LiGaO_2$ and LiAlO2 substrates with a self-separation mechanism. The GaN substrate was single crystal and a smooth surface was created without mechanical or chemical treatment. It was also shown that single crystal GaN could be deposited on Si by a low temperature process. Measurements revealed that the thin compliant SiO_x layer was an effective intermediate layer for the GaN film grown epitaxially on Si.

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