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Nitride-based laser diodes by plasma-assisted MBE—From violet to green emission

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ABSTRACT

We present recent progress in growth of nitride-based laser diodes (LDs) and efficient light-emitting diodes (LEDs) made by plasma-assisted MBE (PAMBE). This technology is ammonia free, and nitrogen for growth is activated by RF plasma source from nitrogen molecules. The recent demonstration of CW blue InGaN LDs has opened a new perspective for PAMBE in optoelectronics. The LDs were fabricated on low threading dislocation density (TDD) bulk GaN substrates at low growth temperatures 600–700 °C. In this work, we describe the nitride growth fundamentals, the influence of the TDD on the layer morphology, the peculiarities of InGaN growth as well as properties of LEDs and LDs made by PAMBE.

1. Introduction

The potential associated with nitride-based light-emitting diodes (LEDs) and laser diodes (LDs) for solid-state lighting has generated a continuing interest in group III-N materials and their alloys. Until very recently, the key achievements and developments in the field of InGaN laser diodes have been made by the metal-organic vapour-phase epitaxy (MOVPE) technique [1,2]. In spite of many potential advantages for MBE growth, such as *in situ* monitoring techniques [3–5], the low quantum efficiency of MBE-grown optoelectronic structures compared with MOVPE led many researchers to conclude that MBE cannot compete with MOVPE. It was also commonly believed that the only solution for MBE would be to bring the growth conditions as close as possible to the MOVPE, i.e. to apply high growth temperatures (~1050 °C for GaN) and high nitrogen precursor overpressure. Indeed, ammonia MBE, which uses atomic beams for group III elements coupled with a large excess supply of NH_3 as the nitrogen precursor [3,4], has been successful in improving the optical quality of nitride films and recently produced the first room-temperature continuous wave (CW) operation of a 405 nm LDs [6]. However, the corrosive nature of ammonia compounded by its large flows creates additional hazards and technological challenges, and also leads to undesirable high hydrogen background during the epitaxial process. In the more widely employed plasma-assisted MBE (PAMBE) [5], purified nitrogen gas is activated using an RF-plasma and supplied to the growth surface at typical flow rates of 1–2 sccm. Early experimental results [7] showed that unlike ammonia MBE, PAMBE requires group III-rich conditions to achieve good material quality. Much progress has been made in both theoretical [8,9] and experimental [10–13] understanding of the growth kinetics for such metal-rich conditions. In spite of the relatively low growth temperatures, 650–750 °C, state-of-the-art GaN/AlGaN heterostructures with record high mobilities of two-dimensional electron gas [14–16] have been grown with PAMBE, making it the technique of choice for the production of electronic devices. Although, sustained refinement of the PAMBE growth conditions on GaN/sapphire MOVPE templates allowed the demonstration of promising LED devices [17], it was the introduction of high-quality GaN substrates which led to dramatic improvements in the optical quality of PAMBE-grown structures, resulting in the room-temperature high-power pulsed and CW blue–violet lasers [18,19]. This paper reports on the progress made by PAMBE in the area of optoelectronic devices, which demonstrates the potential of this technology.

2. Experimental procedure

The growth of all nitride structures presented in this paper was performed in a customized VG90 Oxford MBE reactor equipped with a Veeco RF plasma source (operating at 240 W for 0.8 sccm

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N_2 flow). The pressure during growth was 1.5×10^{-5} Torr. The substrates used were either high-pressure-grown bulk GaN [20] or GaN/Al_2O_3 templates made by MOVPE. The epi-ready bulk substrates were prepared either in a three-step process of mechanical polishing, dry etching, and deposition of a 2 μm GaN:Si buffer layer in the MOVPE reactor or by the two-step procedure: mechanical polishing and mechano-chemical polishing. The back surfaces of the substrates were coated with a 0.7 μm molybdenum layer to improve the thermal coupling for radiative heating. Special holders capable of accommodating small, irregularly shaped substrates, and designed to minimize edge effects ensured high temperature uniformity across the entire substrate area. The typical size of GaN bulk high-pressure substrates was 4 mm × 5 mm, while MOVPE GaN/Al_2O_3 templates were 10 mm × 10 mm. All layers discussed in this paper were grown on the (0 0 0 1) Ga-polarity surface.

3. Growth conditions for PAMBE

The analysis of experimental data for GaAs or Si indicates that the optimum growth temperature for 2D step-flow mode equals about half of the melting temperature, T_M [21,22]. This rule is also valid for GaN growth, where the GaN melting point lies somewhere between 2540 K (experimentally determined for 6 GPa [23]) and 2800 K (theoretically calculated [24]), and the optimum growth temperature used in MOVPE is in the range 1050–1100 °C (1320–1370 K). On a microscopic scale, at $T = 0.5 \cdot T_M$ atomic kinks start to become active, i.e. atoms can detach from an atomic kink [21,22] at a rate comparable to typical attachment rates during deposition. This rule is strict for Kossel crystal and is also fulfilled for real crystal structures.

The difficulty for GaN growth in MBE is that for temperature $0.5 \cdot T_M = 1320$ K, a high nitrogen overpressure (about 60 bars for N_2) is required to prevent GaN decomposition (see Fig. 1) [25,26]. For more chemically active N precursors, like ammonia, the situation is better, but still an overpressure in the range 0.1–2 bar must be used. Such overpressures are not compatible with MBE technology, which relies on high vacuum conditions for the delivery of atoms from the effusion cells to the growing layer. Gallium nitride is a strongly bonded compound (with bonding energy of 9.12 eV/atom pair [27]) compared with typical III–V semiconductors like GaAs (bonding energy of 6.5 eV/atom pair [27]). Consequently, the free energy of the crystal is very low in relation to the reference state of free N and Ga atoms. On the other hand, the N_2 molecule is also strongly bonded (4.9 eV/atom). Therefore, the free energy of GaN constituents at their normal states, Ga and N_2, is quite close to that of the crystal. This is illustrated in Fig. 2, in which the free energy of GaN (1 mole) and the free energy of the system of its constituents (Ga+1/2N_2) is shown as a function of temperature and N_2 pressure. With increasing temperature, the composite Gibbs free energy of the constituents $G_{Ga+1/2N_2}(T)$ decreases faster than $G_{GaN}(T)$ of the crystal, and at higher temperatures, the nitride becomes thermodynamically unstable. The crossing of $G(T)$ curves determines the equilibrium temperature at which GaN coexists with its constituents at given N_2 pressure. The application of pressure increases the free energy of the constituents to a much higher degree than $G(T)$ of the crystal. As a consequence, the equilibrium point shifts to higher temperatures and GaN stability range is extended.

In fact, for typical MBE growth conditions GaN begins to decompose rapidly at temperatures above 800 °C, restricting the epitaxy to temperatures much below the optimum point. Indeed, due to the arguments given above and the low diffusivity of N adatoms, the early efforts to grow GaN in MBE at temperatures below 800 °C, using group V-rich conditions typical for III–V epitaxy, gave unsatisfactory results. These early difficulties, seemingly well grounded in the simple thermodynamics of the processes involved, led many to believe that the only path for successful growth of nitrides in MBE reactors is to push the growth conditions as close as possible to those present in MOVPE reactors.

The breakthrough in the study of growth kinetics in PAMBE came with the finding that, in Ga-rich conditions, it is possible to grow relatively smooth layers at low growth temperatures [7,10–14,16]. However, such growth conditions were prone to the formation of Ga droplets on the GaN surface and high-quality material was mainly formed in the regions between the droplets. Further study of the Ga auto-surfactant effect revealed that this problem could be avoided provided the Ga to N flux ratio was maintained in a very narrow range of values: low enough to be just below the formation of the droplets, but high enough to ensure the formation of a metallic Ga bilayer on the Ga polarity surface [10–14,16]. As an example we demonstrate in Fig. 3, the PAMBE-grown GaN surface morphology for N-rich (rough surface—3D growth) and Ga-rich (smooth surface—2D growth) conditions and growth temperature 710 °C.

This apparent conundrum of finding 2D step-flow growth at temperatures significantly lower than $0.5 \cdot T_M$ can be resolved by considering that the decomposition of GaN (and therefore the

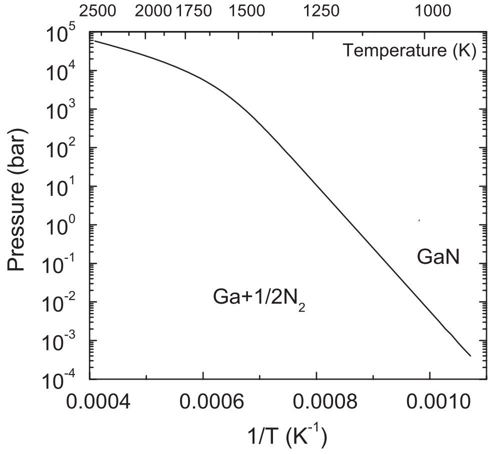

Fig. 1. *p–T* phase diagram of GaN(s)–Ga(l)–N_2(g) system, determined by Karpinski et al. [25,26].

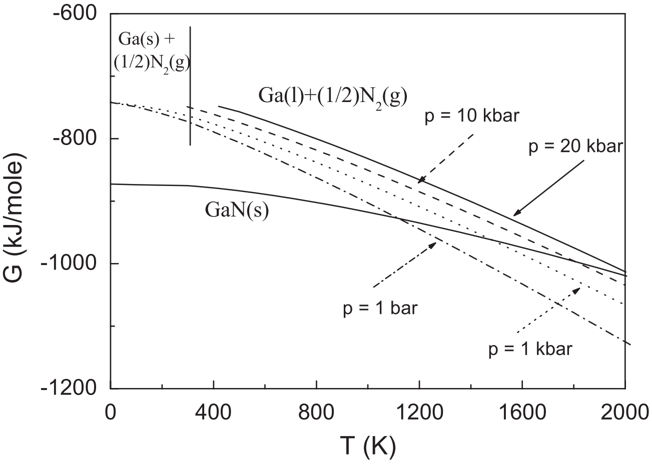

Fig. 2. Gibbs free energy of GaN and its constituents as a function of temperature: Ga+N_2 GaN—thick solid line, the constituents: Ga+N_2–p=1 bar dash—dotted line, p=1 kbar—dotted line, p=10 kbar—dashed line, and p=20 kbar—solid line.