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InN growth by high-pressures chemical vapor deposition: Real-time optical growth characterization

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Abstract

Growth techniques that utilize elevated reactor pressures offer a pathway to overcome limitations in the epitaxy of high quality group III-nitride compounds such as InN or related materials, which exhibit large thermal decomposition pressures. We introduce the growth of InN by a unique high-pressure chemical vapor deposition (HPCVD) system, demonstrating that HPCVD is a valuable method for achieving stoichiometric single-phase surface compositions at optimal processing temperatures. The development and utilization of real-time optical diagnostics for the monitoring of gas-phase and surface chemistry during the heteroepitaxial nucleation and growth is critical for controlling the chemical vapor deposition process. Using real-time optical ultraviolet absorption spectroscopy (UVAS), we have studied the flow and decomposition kinetics of the gas-phase precursors as functions of flow, pressure and temperature. A pulsed-injection technique for the delivery of the chemical precursors is used, enabling the analysis and control of the decomposition kinetics of trimethylindium (TMI) and ammonia as well as the study of the initial stages of InN nucleation and subsequent overgrowth on sapphire substrates. The nucleation and steady state growth of InN is probed with sub-monolayer resolution by principal angle reflectance (PAR) spectroscopy. These real-time optical monitoring techniques demonstrate their utility in the optimization and engineering of the growth process, as well as providing crucial insights into gas phase decomposition dynamics and surface chemistry processes under HPCVD conditions. The resulting InN material exhibits an optical absorption edge that varies from 0.83 to 1.34 eV, strongly dependent upon the precursor flow ratios employed during growth. Structural analysis performed by XRD reveals high quality InN.

Keywords: High-pressure CVD; Gas-phase kinetics; Real-time growth monitoring; InN growth

1. Introduction

The development of integrated ultraviolet (UV) light emitting diodes (LEDs), laser diodes, solar blind detectors, high-frequency/high-power transistors operating at high temperature and room-temperature spintronic devices that are based on group III-nitride compound semiconductors has generated much interest in recent years. Of particular interest is an improved knowledge of the binary base systems InN, GaN and AlN, and to which extent alloys and heterostructures can be employed in the fabrication of optical electronic device structures [1,2]. GaN is the most studied group III-nitride compound, but InN and AlN have become increasingly significant due to their unique properties as low band gap and wide band gap materials, respectively.

At present, the most commonly utilized growth techniques for the production of group III-nitrides are organometallic chemical vapor deposition (OMCVD, also denoted as MOVPE) and molecular beam epitaxy (MBE) [3,4]. However, these low-pressure deposition processes are limited to a temperature range under which the partial pressures of the constituents do not differ vastly and decomposition processes can be countered by off-equilibrium conditions. These off-equilibrium conditions employed in MBE and organometallic CVD growth of InN require a relatively low growth temperatures in order to overcome the thermal decomposition pressures, thus limiting the quality of InN and related group III-nitride epilayers [1,5–7]. In addition, these low growth temperatures require the application of extremely high V–III ratios in order to prevent the formation of metal droplets on the thin film surface. Recent studies pertaining to the decomposition of InN layers [8] have shown that oxygen is easily incorporated into the InN crystal under thermal treatments, and has been suggested as the source for the wide discrepancy in reports in the band gap energy of InN. Controversial reviews of the present status of InN growth and characterization have been provided by Bhuiyan et al. [1] and Davydov et al. [9], implying that different approaches for the

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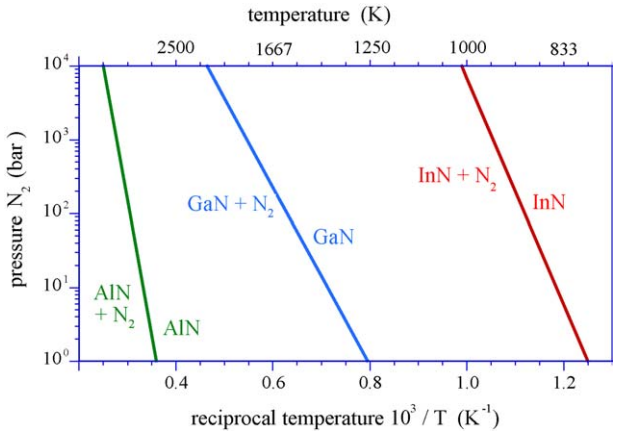

Fig. 1. Thermal decomposition pressure vs. reciprocal temperature for AlN, GaN and InN [11].

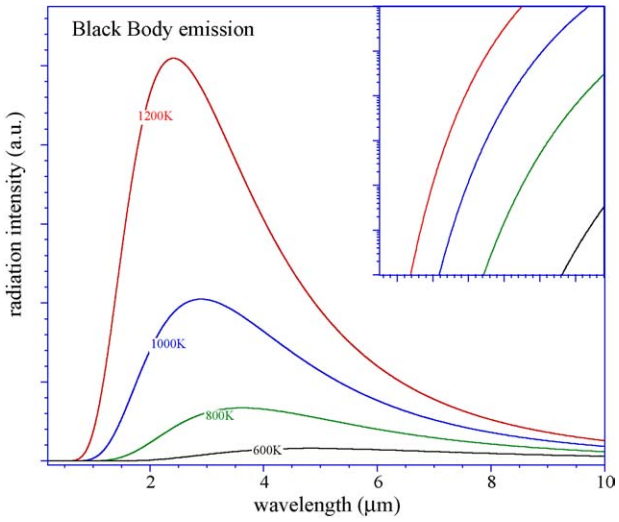

Fig. 2. Intensities and spectral distribution of a black body emitter such as a hot substrate for different temperatures. In inset depict on a logarithmic scale the onset the radiation for 100 and 600 K.

growth of In-rich group III-nitride alloys need to be explored in order to improve the structural and optical properties of InN and related alloys.

Recent studies in the indium-nitrogen system [10] show much uncertainty in the *p–T–x* relations due to missing experimental validation. However, studies of the nitrogen pressure required to prevent thermal decomposition of bulk InN, provide a relationship given by

$$p_{N_2} \rightarrow p_0 \exp\left[-\frac{\Delta H_r}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right], \quad (1)$$

which results in the p–T^{-1} relation shown in Fig. 1 [11]. This relation indicates that for the pressure range $p_{N_2} \leq 10^2$ bar and substrate temperatures ≤ 900 K, the surface decomposition of InN can be effectively suppressed.

The approach presented here explores the growth of indium-rich group III-nitrides at elevated pressures using InN as a model system in order to demonstrate the capabilities of high-pressure CVD. InN is the most challenging material system, since the equilibrium vapor pressure of nitrogen over InN is much higher compared to AlN and GaN [12]. A high-pressure flow channel reactor incorporating real-time optical characterization capabilities [13–16] is utilized to study and optimize InN nucleation and growth. At above atmospheric pressures, optical diagnostic techniques are uniquely suited to provide real-time information pertaining to gas flow dynamics in laminar and turbulent flow regimes. Optical diagnostics are also utilized to obtain crucial information regarding precursor flow and decomposition kinetics. Several optical techniques have been explored, but only a few provide the required robustness and sensitivity. For example, the substrate temperature during InN growth under high pressure is between 800 and 1000 K, resulting in a significant radiation emission, as shown in Fig. 2. Even if modulation techniques are applied, the intensity of the emitted radiation from to the substrate heater limits the sensitivity of many optical probe techniques operating in visible and infra-red (IR) ranges. As depicted in the inset of Fig. 2, the radiated intensity for a 1000 K back body emitter vanishes very quickly below 350 nm, with negligible contributions below 300 nm.

Utilizing ultraviolet absorption spectroscopic (UVAS) techniques as well as UV induced fluorescence spectroscopy to identify the group V and organometallic group III precursors in the gas phase is well established in the literature [17–20].

In the following sections, a brief introduction of the HPCVD reactor design is provided along with its real-time optical capabilities in order to characterize flow, gas phase and surface reactions. This is followed by three sections providing results on the optical characterization of the precursors trimethylindium (TMI) and ammonia (NH_3) and the optical monitoring of InN nucleation and overgrowth utilizing sequential precursor injection.

2. High-pressure reactor system

The growth of group III-nitrides at elevated pressures requires a completely redesigned OMCVD reactor system with special consideration directed towards flow kinetics, gas phase reactions, boundary layer diffusion and alteration of surface chemistry. This HPCVD reactor system utilizes a pulsed precursor injection technique, which is essential in order to achieve compression of the precursors to reactor pressure, minimization of gas phase reactions, optimization of nucleation kinetics, and analysis of gas phase and surface decomposition dynamics in real-time.

A symmetric arrangement of substrates in the upper and lower part of the flow channel is used, in order to prevent preferential material deposition on the opposite side of the heated substrate. As schematically depicted in Fig. 3b, optical access ports are integrated along the center axis of the substrates, which allows optical characterization of flow kinetics, gas phase reactions and the substrate surface through the back side. A more detailed description of the reactor design and the optical characterization capabilities is given elsewhere [13,16].