Journal of Crystal Growth 464 (2017) 127–131

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth of high purity N-polar (In,Ga)N films

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ARTICLE INFO

Communicated by T.F. Kuech

Keywords:
A1. Impurities
A1. Polarity
A1. N-polar
A3. Metalorganic chemical vapor deposition
B1. Nitrides

ABSTRACT

In this work, secondary ion mass spectroscopy was used to study carbon and oxygen impurity incorporation in N-polar [000–1] GaN films grown by MOCVD. The effects of growth temperature, V/III ratio, and precursor flows were studied within a regime relevant to low temperature (In,Ga)N:Mg growth for device structures containing high indium concentrations. For films grown without magnesium, oxygen levels were between 3 and 8×10^{16} cm^{-3} and did not depend strongly on the growth conditions. Mg-doped films yielded higher oxygen concentrations ranging from 8×10^{16} to 4×10^{17} cm^{-3} depending on the gallium and magnesium precursor flow rates. The carbon concentration in the films varied significantly with different growth conditions, and was most affected by the growth temperature and the V/III ratio. With careful tuning of the growth parameters carbon and oxygen concentrations of 2 and 4×10^{16} cm^{-3}, respectively, were achievable under a wide range of conditions.

1. Introduction

While most commercial GaN devices are grown in the [0001] c-orientation, other crystallographic orientations are attractive for polarization-engineered heterostructures. Semipolar and nonpolar devices have shown significant potential in light-emitting applications due to the reduced polarization-induced quantum confined Stark effect (QCSE) in these orientations [1,2], and some semipolar planes have been shown to have higher indium uptake efficiencies compared to c-plane growth [3]. The [000–1] N-polar orientation has a reversed polarization direction compared to the [0001] Ga-polar orientation and is attractive for many devices that can benefit from the reversed polarization fields, such as GaN/AlGaN high electron mobility transistors (HEMTs), solar cells, photodetectors, GaN/InGaN/GaN tunnel diodes, light emitting diodes (LEDs), and lasers [4,5]. In addition to the reversed polarization direction, the N-polar orientation has a higher indium incorporation efficiency than the Ga-polar orientation [6] making it attractive for devices that require high indium content layers such as long wavelength emitters and InGaN tunnel diodes. For these devices, growth of the active region and subsequent layers must be performed at low temperatures to avoid indium desorption and thermal degradation of the InGaN layers. When growing at low temperatures, additional care must be taken to decrease unintentional impurity incorporation.

While smooth Ga-polar films can be grown on on-axis c-sapphire wafers, growth in the N-polar direction is typically conducted on miscut substrates to promote a smooth surface morphology over a wide range of growth conditions [7]. In the past N-polar layers have been shown to have increased oxygen incorporation compared to Ga-polar films [8]. More recently, N-polar films with residual oxygen contents as low as 2×10^{16} cm^{-3} have been reported for smooth GaN films grown on miscut substrates at high growth temperatures under optimized conditions [4]. At reduced growth temperatures, however, increased oxygen content had again been observed in addition to elevated carbon impurity incorporation in layers grown with trimethyl gallium as precursor, due to incomplete removal of methyl groups from the growing surface [9]. The carbon incorporation could be suppressed when using triethyl gallium as precursor [4], due to the easier removal of ethyl groups via β-elimination [10].

Both oxygen and carbon incorporate predominantly on the nitrogen sites in GaN, forming shallow donor and deep acceptor states respectively [11–13]. While oxygen itself is a shallow donor, it can also exist in complexes with Ga-vacancies. In the case of carbon, both isolated carbon and C-V_{Ga} complexes form deeper states in the band gap. Since these impurity states can significantly impact device performance, it is important to be able to understand and control the levels of these unintentional dopants.

Here we present a comprehensive study on the interplay of precursor selection and growth conditions on impurity incorporation over a wide range of growth parameters compatible to the (In,Ga)N growth regime.

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http://dx.doi.org/10.1016/j.jcrysgro.2016.11.039

Available online 14 November 2016

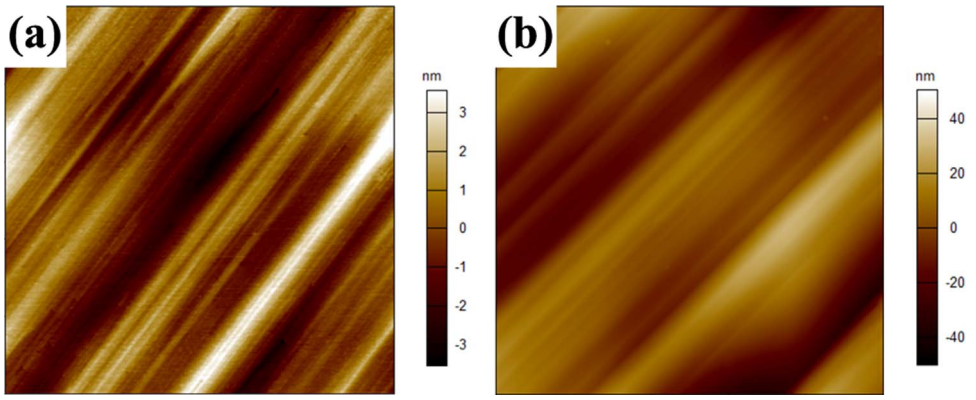

Fig. 1. 5×5 μm^2 AFM scans showing the sample surface after (a) GaN template growth and (b) growth of a 2 μm thick SIMS stack.

2. Experimental

While the focus of this report is to study impurity incorporation in the low temperature (In,Ga)N growth regime, it is difficult to grow thick InGaN layers for SIMS analysis since in the N-polar orientation hexagonal hillocks tend to form during the growth of thick layers in nitrogen ambient, even when grown on misoriented substrates [4]. These irregular surface features will affect the impurity incorporation, due to step bunching and the presence of multiple crystallographic facets. In order to avoid morphological degradation and to maintain step-flow growth, all (In,Ga)N layers in the SIMS stacks in this study were grown in the presence of 1 slm hydrogen. As the presence of hydrogen suppresses indium incorporation, the indium content in layers grown in the presence of TMIn was below 4% for all layers studied. Using this technique, thick layer stacks up to around 2 μm could be grown while maintaining morphologies similar to the original templates used (Fig. 1a and b). While the RMS roughness of the stacks increased from 1.3 to 12.3 nm for a 5×5 μm^2 area due to the thick layer growth, no additional crystallographic features such as hillocks were formed. A similar approach was pursued in previous studies, which also showed that the C and O impurity incorporation was independent of the carrier gas used (H_2/N_2). In addition the investigations confirmed that the impurity concentration in InGaN/GaN MQW stacks, where the $In_{0.2}Ga_{0.8}N$ wells were grown in pure N_2 was similar to the impurity levels in such MQW stacks where H_2 was added during InGaN well deposition, resulting in a negligible indium content in the wells, similar to the growth conditions in this study [4]. For these reasons it is assumed that the impurity incorporation discussed herein will apply to all layers grown in the presence of TMIn in the gas phase, regardless of the indium content in the layers.

The substrates used in this study were c-sapphire miscut 4 degrees towards the a-direction, resulting in a GaN layer miscut toward the GaN m-direction. Substrates were loaded into an atmospheric pressure two-flow MOCVD reactor (equipped with a load-lock) and template growth was initiated with a high temperature nitridation step, followed by nucleation layer growth and deposition of a thick 1 μm GaN layer at 1200 °C. Fig. 1a shows the surface morphology of the resulting template, with a RMS roughness of 1.3 nm for a 5×5 μm^2 image. Further details of the template growth and their properties have been presented elsewhere [4,7]. Next, layer stacks were grown at different temperatures (750–950 °C), trimethyl gallium (TMGa, 0–9.0 μmol/min), triethyl gallium (TEGa, 0–6.5 μmol/min), trimethyl indium (TMIn, 0–56 μmol/min), bis-cyclopentadienyl magnesium (Cp_2Mg, 0–0.69 μmol/min), and NH_3 flows (1–6 slm). A variety of different combinations of precursors were used, and when not otherwise mentioned the standard flows were 3.2 slm NH_3, 4.6 μmol/min TEGa, 6.5 μmol/min TMGa, 0.12 μmol/min Cp_2Mg, and 37 μmol/min TMIn with only one parameter varied for each series of layers presented. For a TEGa flow of 4.6 μmol/min and a TMGa flow of 6.5 μmol/min, the corresponding growth rates were 0.7 Å/s and 0.8 Å/s respectively and the growth rate was only dependent on the Ga source molar flow in the range studied, independent of all other growth parameters. The around 200-nm-thick layers of interest were separated by at least 100-nm-thick Si-doped spacer layers so that each layer could be easily identified. High purity precursors and gases were used to minimize impurity incorporation. Secondary ion mass spectroscopy (SIMS) analysis was performed on all samples by Evans Analytical Group. The detection limits for each species were as follows: carbon, 1×10^{16} cm^{-3}; oxygen, 1×10^{16} cm^{-3}.

3. Results and discussion

3.1. Oxygen incorporation

Fig. 2 illustrates the oxygen concentration determined by SIMS for GaN layers grown under a variety of conditions. As expected from the higher stability of Ga_2O_3 at reduced temperatures, the O content slightly increased from 3 to 4×10^{16} cm^{-3} to 6×10^{16} cm^{-3} when the growth temperature was decreased from 950 to 750 °C for layers grown with a V/III ratio of 28,000, as shown in Fig. 2a. For layers grown using only TEGa or TMGa with a NH_3 flow of 3.2 slm the oxygen concentration was largely independent of the Ga precursor flow, ranging between 4 and 6×10^{16} cm^{-3} (Fig. 2b). Since O occupies the N site in GaN, the oxygen content in the layers decreased from to 9×10^{16} cm^{-3} for films grown with a V/III ratio of 9000 to values between 4 and 6×10^{16} cm^{-3} at higher V/III ratios above 18,000 (higher NH_3 flows) due to the higher N overpressure in the gas phase (Fig. 2c). When TMIn was added to the gas phase no marked change in the oxygen incorporation was observed.

In p-type GaN:Mg films, the O content in the layers increased sharply upon the addition of 0.02 μmol/min Cp_2Mg into the gas phase, and increased further for higher Cp_2Mg flows (Fig. 2d). The additional O incorporation in the presence of Mg can be explained by the higher bond strength of 394 kJ/mol between Mg and O compared to 285 kJ/mol for the Ga–O bond. At a constant Mg flow, the O incorporation was largely independent of growth temperature and V/III ratio in the investigated regime, ranging from 8×10^{16} cm^{-3} to 1×10^{17} cm^{-3} (Fig. 2a and c). Finally, as the TEGa flow was increased in the presence of Cp_2Mg the O level decreased for higher TEGa flows. Since the Cp_2Mg flow was kept constant as the TEGa flow was increased, this led to a lower fraction of Mg in the gas and solid phases and thus a lower fraction of Mg-O bonds formed compared to Ga-O bonds, which dissociate more readily (Fig. 2b). These results indicate that while films with low oxygen content can be grown under a variety of growth conditions, oxygen levels are weakly dependent on the growth temperature and V/III ratio and can be most effectively controlled by using a low Mg:Ga ratio.