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Atomic layer deposition of GaN at low temperatures

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The authors report on the self-limiting growth of GaN thin films at low temperatures. Films were deposited on Si substrates by plasma-enhanced atomic layer deposition using trimethylgallium (TMG) and ammonia (NH_3) as the group-III and -V precursors, respectively. GaN deposition rate saturated at 185 °C for NH_3 doses starting from 90 s. Atomic layer deposition temperature window was observed from 185 to ∼385 °C. Deposition rate, which is constant at ∼0.51 Å/cycle within the temperature range of 250 – 350 °C, increased slightly as the temperature decreased to 185 °C. In the bulk film, concentrations of Ga, N, and O were constant at ∼36.6, ∼43.9, and ∼19.5 at. %, respectively. C was detected only at the surface and no C impurities were found in the bulk film. High oxygen concentration in films was attributed to the oxygen impurities present in group-V precursor. High-resolution transmission electron microscopy studies revealed a microstructure consisting of small crystallites dispersed in an amorphous matrix. © *2012 American Vacuum Society*.
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I. INTRODUCTION

III-nitride compound semiconductors (AlN, GaN, and InN) and their alloys are promising materials for a wide range of electronic and optoelectronic device applications.[1] Although high quality epitaxial films of these nitrides can be grown by metal-organic chemical vapor deposition (MOCVD), temperature-sensitive device layers and substrates used in novel devices necessitate the adaptation of low-temperature growth methods. Atomic layer deposition (ALD) is a low-temperature chemical vapor deposition method, which offers unique advantages such as high uniformity, conformality, and sub-nanometer thickness control due to its self-limiting growth mechanism.[2]

Growth of GaN thin films by atomic layer epitaxy (ALE) using triethylgallium ($Ga(C_2H_5)_3$),[3] trimethylgallium ($Ga(CH_3)_3$),[4] and gallium trichloride ($GaCl_3$),[5] has been reported for temperatures above 450 °C. Lower growth temperatures (350 – 400 °C) were achieved when GaCl was used as the gallium precursor.[6] Sumakeris *et al.*[7] reported growth of GaN films within the temperature range of 150 – 650 °C by using a novel reactor design that employs hot filaments to decompose the ammonia. Recently, Kim *et al.*[8] deposited GaN thin films by thermal ALD using $GaCl_3$ and NH_3 precursors. In their study, growth rate saturated at ∼2.0 Å/cycle within the temperature range of 500 – 750 °C for $GaCl_3$ and NH_3 doses of (7 s, 50 sccm) and (10 s, 500 sccm), respectively.

In this work, we demonstrate the self-limiting growth of GaN thin films via plasma-enhanced ALD (PEALD) within the temperature range of 185 – 385 °C, using TMG and NH_3 as the group-III and -V precursors, respectively.

II. EXPERIMENT

GaN thin films were deposited on precleaned Si substrates at temperatures ranging from 100 to 500 °C. Depositions were carried out in a load-locked Fiji F200 ALD reactor (Cambridge Nanotech) with a base pressure of 0.25 torr, using Ar as the carrier gas. Trimethylgallium was kept at room temperature. NH_3 plasma flow rate and power were 50 sccm and 300 W, respectively. System was purged for ten seconds after each precursor exposure. Prior to depositions, solvent-cleaned substrates were dipped into dilute HF solution for ∼1 min, then rinsed with DI-water and dried with N_2.

Film thicknesses were measured by using variable angle spectroscopic ellipsometry (VASE, J.A. Woollam). Ellipsometric spectra of the samples were recorded *ex situ* at three angles of incidence (65°, 70°, 75°) in the wavelength range of 400 – 1200 nm. Optical constants of a ∼17 nm thick GaN thin film deposited at 250 °C was modeled by the Cauchy dispersion function, and used for the estimation of PEALD-grown film thicknesses. Thermo Scientific K-Alpha spectrometer with a monochromatized Al Kα x-ray source was used for the x-ray photoelectron spectroscopy (XPS) studies. Grazing-incidence x-ray diffraction (GIXRD) measurements were performed in a PANanalytical X'Pert PRO MRD diffractometer using Cu Kα radiation. FEI Tecnai G2 F30 transmission electron microscope (TEM) was used for the imaging of samples prepared by FEI Nova 600i Nanolab focused ion beam (FIB) system. Surface morphology was investigated by using atomic force microscopy (AFM) (Asylum Research, MFP-3D).

III. RESULTS AND DISCUSSION

Effect of TMG dose on the deposition rate was investigated at 185 °C with a constant NH_3 flow duration of 40 s [Fig. 1(a)]. Trimethylgallium doses of 0.015 and 0.03 s resulted with the same deposition rate, i.e., 0.46 Å/cycle; indicating that 0.015 s is high enough for saturative surface reactions to take place. Figure 1(b) shows GaN deposition rate as a function of NH_3 flow duration. Trimethylgallium dose and NH_3 flow rate were constant at 0.015 s and 50 sccm, respectively. Deposition rate increased with NH_3 flow

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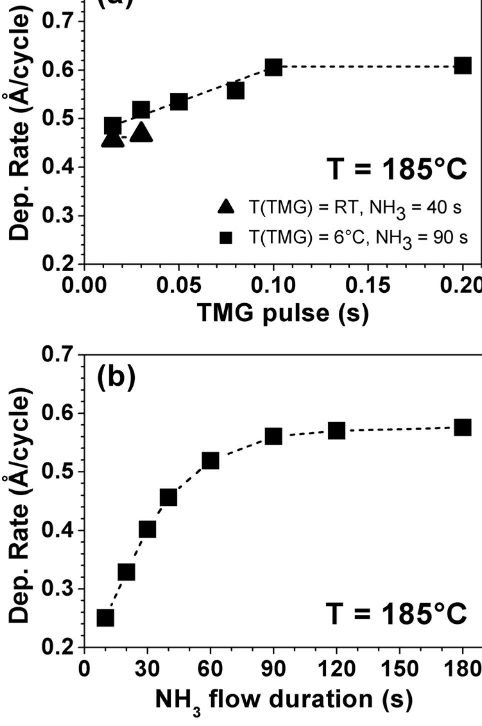

FIG. 1. (a) Trimethylgallium saturation curves at 185 °C for different TMG temperatures. NH_3 flow rate was constant at 50 sccm. (b) NH_3 saturation curve at 185 °C. Trimethylgallium dose was constant at 0.015 s.

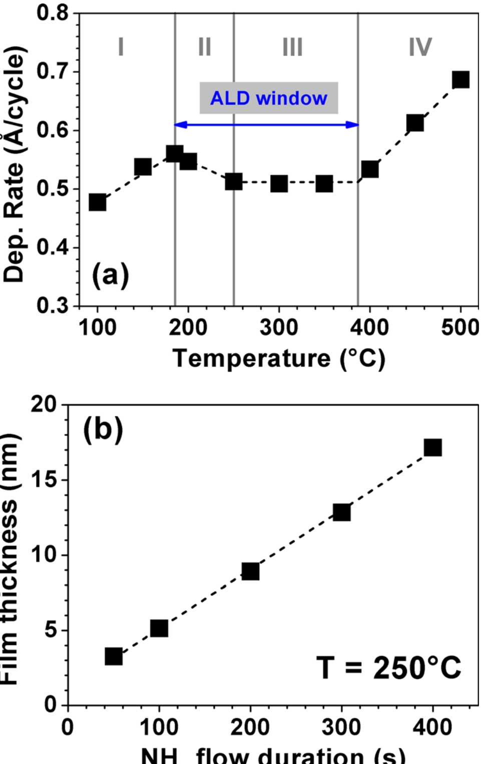

FIG. 2. (Color online) (a) Deposition rates of GaN thin films at different temperatures. (Trimethylgallium was at room temperature.) (b) Film thickness vs number of deposition cycles.

duration until 90 s and reached saturation at ~0.56 Å/cycle. By using the saturation value of NH_3 exposure step (50 sccm, 90 s), saturation behavior of TMG was restudied. Since TMG has a very high vapor pressure at room temperature, precursor was cooled down to 6 °C and stabilized at this temperature prior to depositions. The results are given in Fig. 1(a). Deposition rate increased with TMG dose within the range of 0.015 – 0.1 s. For 0.1 s and higher TMG doses, saturation was observed at ~0.61 Å/cycle. In order to determine the temperature range at which the deposition rate is constant (i.e., the ALD window), 100 cycles with 0.015 s TMG and 90 s NH_3 plasma were deposited at different temperatures. Deposition rate versus temperature graph consisted of four distinct regions [Fig. 2(a)]. Deposition rate was constant at ~0.51 Å/cycle in region III (250 – 350 °C), implying that the growth of GaN at these temperatures is self-limiting. For temperatures in the range of 185 – 250 °C (region II), deposition rate increased with decreasing temperature. Deposition rate was ~0.56 Å/cycle at 185 °C. In order to investigate the effect of purging duration at this temperature, an experiment has been carried out by doubling the purge time. Deposition rate obtained by using 20 s purge time was same as that obtained by using 10 s. Although deposition rate has an obvious temperature dependency in region II, both TMG and NH_3 precursors showed saturation behaviors at 185 °C. Since growth was proven to be self-limiting at 185 °C, region II has been also included to the ALD window. Region I (100 – 185 °C) corresponds to the activation energy limited zone, where deposition rate decreases at low temperatures due to the decrease in thermal energy. For ~385 °C and higher temperatures (region IV) growth rate increased with temperature, which is probably due to the decomposition of TMG. Depending on these observations, upper and lower limits of the ALD window, in which surface reactions take place in a self-limiting fashion, were estimated as ~385 °C and 185, respectively. Film thickness versus number of deposition cycles at 250 °C is given in Fig. 2(b). Film thickness increases linearly with the number of cycles, confirming that the deposition rate is constant at this temperature due to the self-limiting nature of the ALD process.

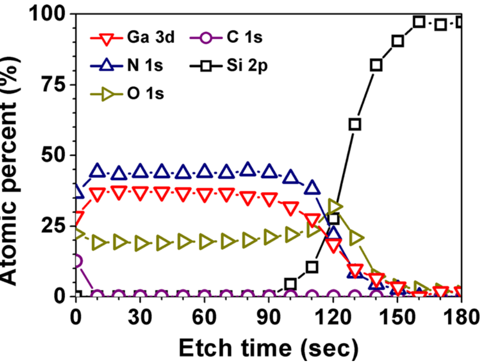

FIG. 3. (Color online) XPS depth profile of ~17 nm thick GaN thin film deposited at 250 °C.

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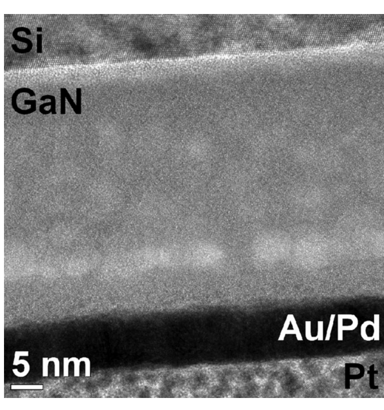

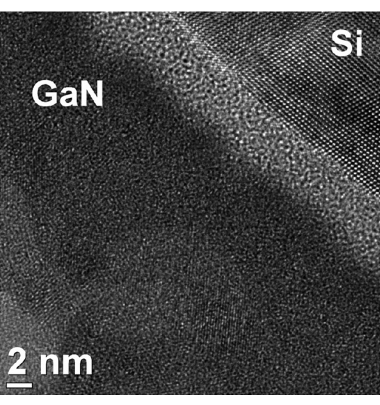

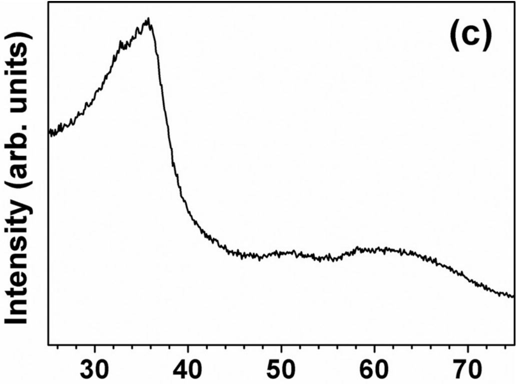

FIG. 4. (a), (b) Cross-sectional HR-TEM images of ~41 nm thick GaN thin film deposited at 185 °C on Si (111) substrate. (b) GIXRD pattern of ~17 nm thick GaN thin film deposited at 250 °C on Si (100) substrate.

Compositional characterization of ~17 nm thick GaN film was carried out by using XPS. Survey scan detected peaks of gallium, nitrogen, oxygen, and carbon. Figure 3 represents the compositional depth profile of the film deposited at 250 °C. In the bulk film (etch time = 60 s), concentrations of Ga, N, and O were 36.6, 43.9, and 19.5 at. %, respectively. Compositional characterization of ~41 nm thick film deposited at 185 °C revealed similar results, where concentrations of Ga, N, and O in the bulk film were determined as ~31.3, ~46.9, and ~21.8 at. %, respectively. As the deposition temperature decreased from 250 to 185 °C, oxygen content in the film increased from ~19.5 to ~21.8 at. %. This behavior is similar to that seen in the case of deposition rate, and may explain the higher deposition rates observed in region II [Fig. 2(a)]. For both of these films, carbon was detected only at the surfaces and no C impurities were found in the bulk films, indicating that the methyl groups (CH_3) were completely removed from TMG molecules by the use of NH_3 plasma. Constant oxygen concentrations throughout the film thicknesses reveal that the oxidation occurs during film deposition. In order to determine the source of oxygen present in the films, trimethylaluminum (TMA) precursor (carried by Ar) was pulsed into the reactor for 500 times at 250 °C. There was 10 s purging time between the pulses. If there were any unwanted oxygen contents in the reactor or in the Ar gas, then Al_2O_3 would be expected to grow. However, no film growth was observed. A similar experiment was carried out at 185 °C using the TMG precursor. Trimethylgallium (carried by Ar) was pulsed into the reactor for 300 times. The reactor was purged for 10 s after each pulse. Again, no film growth was observed. These results indicate that the source of oxygen is neither a leak in the reactor nor the Ar gas. The most probable source of high oxygen levels is the O-containing impurities in ammonia (NH_3) gas. This argument strengthens by the fact that there are no filters/gas purifiers attached to this line.

High-resolution TEM (HR-TEM) images of ~41 nm thick GaN thin film deposited at 185 °C are given in Figs. 4(a) and 4(b). Film thickness was measured as 40.8 nm from Fig. 4(a), which is in good agreement with the results obtained by spectroscopic ellipsometry. Film was found to be composed of small crystallites dispersed in an amorphous matrix [Fig. 4(b)]. A similar microstructure was also observed for the ~17 nm thick GaN thin film deposited at 250 °C (not shown here). GIXRD pattern of this sample [Fig. 4(c)] indicates an amorphous structure, with some implications of long-range order corresponding to the small crystallites that exist in the amorphous Ga-O-N matrix.

Surface morphology of the film was studied by AFM. Root-mean-square roughness (rms) of the ~17 nm thick film deposited at 250 °C was measured as ~0.58 nm from a 1 μm × 1 μm scan area.

IV. SUMMARY AND CONCLUSIONS

GaN thin films were deposited via PEALD at temperatures ranging from 100 – 500 °C. Atomic layer deposition temperature window was observed from 185 to ~385 °C. Deposition rate, which is constant at ~0.51 Å/cycle within the temperature range of 250 – 350 °C, increased slightly as the temperature decreased to 185 °C. Although deposition rate has an obvious temperature dependency within the range of 185 – 250 °C, growth was proven to be self-limiting at these temperatures. Film thickness versus number of cycles plot exhibited a linear behavior (i.e., constant deposition rate) at 250 °C. Concentrations of Ga and N were constant at ~36.6 and ~43.9 at. % through the film thickness. ~19.5 at. % O present in the bulk film was attributed to the oxygen impurities in group-V precursor. High-resolution TEM images of GaN thin film deposited at 185 °C showed small crystallites dispersed in an amorphous matrix.

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