The properties and deposition process of GaN films grown by reactive sputtering at low temperatures

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Polycrystalline gallium nitride films, 100 nm to 1 μm thick, were deposited under a range of conditions. Substrate electrode temperatures during sputtering were varied from room temperature to 450 °C, the pressure from 0.15 to 6.0 Pa, the nitrogen fraction of the deposition atmosphere from 10% to 100% and the target bias from -400 to -1800 V. The deposition rates as functions of these conditions are in the range 0.5–25 nm/min. The growth rate is considered to be controlled respectively by the thermally activated desorption from the substrate, changes in the mean free path and concentration of gas particles, differences between the sputter yields of Ga and GaN in Ar and N_2 , and changes in the ion current and sputter yields. The films are generally columnar, with the grain size increasing with film thickness. The most crystalline films were grown at mid range temperatures, low N_2 concentrations, and low target biases, and the most disordered were grown at low pressures. The latter two cases suggest that decreasing the energy of particles incident on the film during deposition results in a more ordered film. The biaxial stress is compressive and shows an increasing trend with the target bias and N_2 concentration, reaching 4.7 GPa at 75% N_2 . Oxygen contamination of 3–30 at. % has a major effect on the optical properties of the films, increasing the band gap values from 3.02 to >4.0 eV and the Urbach tail energies from around 150 to 840 meV and decreasing the refractive index from 2.46 to 2.03. At a 40% N_2 deposition fraction, the N:Ga ratio is more or less constant at 1:1. Since the absolute oxygen incorporation rate changes very little, it is the relative film deposition rate which determines the final oxygen concentration. Excess Ga at low N_2 concentrations causes a decrease in the band gap and an increase in the Urbach tail energy.

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I. INTRODUCTION

In recent years, crystalline GaN and related semiconductors have received much attention for short-wavelength optoelectronic devices and have also found use in a number of other applications. Most materials are epitaxially grown on a variety of substrates, typically sapphire or SiC ,¹ and at high temperatures. This is done by a variety of techniques, including chemical-vapor deposition (CVD), molecular beam epitaxy (MBE), and vapor-phase epitaxy (VPE). Although rf sputtering is comparatively inexpensive, there have been few reports of epitaxially grown, single crystal GaN using this method.^{2,3} This technique has much more often been used to grow polycrystalline and amorphous materials.^{4–11} These films, using N_2 as the reactive gas and Ar or N_2 to sputter a Ga target, are usually grown at low temperatures (≤ 450 °C). A disordered material grown at low temperatures using remote-plasma CVD has been shown to have potential for lighting and photodiode applications.^{12,13}

However, these studies only investigate the effect of changing one and sometimes two of the major sputter-deposition parameters in a controlled manner. In addition, attention is seldom paid to the deposition itself and to the level of oxygen contamination.

The main objective of this experiment is to study how the four main controllable parameters in the given rf sputter-

ing system affect the structural, chemical, and optical properties of the deposited films, and how these parameters affect the actual deposition process.

II. EXPERIMENT

A. Growth

GaN films were deposited using a Nordiko conventional rf reactive sputtering system operating at 13.56 MHz. The target was 99.9999% pure Ga, contained in a Ni dish on the lower driven electrode which was water cooled. The substrates were attached to the upper electrode by means of steel clips. The substrates used were (001) Si and fused quartz, and these were degreased with organic solvents prior to deposition. The substrate electrode was electrically grounded and could be heated to 450 °C.

The growth chamber was fed by Ar and N_2 gas lines (99.9999% purity), and the flow rates controlled by 20 SCCM (standard cubic centimeter per minute) mass-flow controllers. A quartz shield surrounded the region between the two electrodes containing the plasma. Before each deposition, the chamber and gas lines were evacuated to a pressure below 3×10^{-4} Pa by a rotary/diffusion pump combination.

The influence of varying the substrate electrode temperature, the deposition pressure, the N_2 :Ar gas ratio, and the target self-bias on the properties of the resulting films was investigated. During a *standard* deposition, the parameters

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were kept at room temperature, 2.0 Pa, 8:12 SCCM (40% N₂), and -800 V. One parameter was varied at a time, and the changes in the films' properties were measured. Deposition times were adjusted to keep the film thickness close to 100 nm to allow a better comparison between the various properties. A few thicker films, up to 1 μm, were also grown for comparison.

B. Measurements

Film thicknesses were measured using profilometry and ellipsometry at a 632.8 nm wavelength. Ellipsometry was also used to obtain values for the refractive index. The surface was imaged using a Hitachi S4000 scanning electron microscope (SEM). The surface topography was analyzed using a Digital Instruments, Dimension 3100 atomic force microscope (AFM) operating in the tapping mode. The cross-sectional transmission electron microscopy (TEM) was carried out in a Philips CM200. The relative elemental composition of the films was measured using energy dispersive X-ray (EDX) spectroscopy on a Philips XL30 SEM. Optical absorption spectra of samples deposited on quartz substrates were measured with a Camspec M300 UV-visible spectrophotometer. The biaxial stress was estimated from profilometric measurements of the change in curvature of Si substrates utilizing Stoney's equation. The absorbance spectra of the films were obtained by subtracting the absorbance of the substrate from the total absorbance. Optical band gaps were estimated by extrapolating linear fits to plots of the absorption coefficient α squared versus the photon energy $h\nu$ at the band edge, the standard method for crystalline, direct band gap materials. Urbach tail energies were obtained from the inverse of the gradient of $\ln \alpha$ vs $h\nu$ at the band tail.

III. RESULTS AND DISCUSSION

A. General

Films deposited under standard conditions on quartz have a yellowish tinge. The films become much darker as the nitrogen fraction of the deposition gas is reduced to 10% and slightly darker when the target bias voltage is increased to very high values. At very low biases, the films appear almost clear and glass like. At N₂ fractions of 60% and above, the films on Si tend to delaminate. The Ga target sometimes melts at high rf powers or during long deposition runs, but the deposition rates are not reduced as would be expected as a result of energy loss in the liquid.¹⁴

B. Deposition rate

The deposition rate was calculated by dividing the thickness of the GaN film on Si by the deposition time. These values are plotted in Fig. 1 as functions of the deposition conditions. Profilometric values were used when ellipsometry proved unreliable because of the absorption at the laser wavelength or delamination.

1. Dependence on substrate electrode temperature

As the substrate electrode temperature is increased, the deposition rate remains approximately constant at around

FIG. 1. Deposition rate as a function of deposition conditions.

3.8 nm/min until 150 °C, after which it decreases with temperature, reaching 1.3 nm/min at 450 °C. Factors which may affect the deposition rate include the adsorption and desorption rates of Ga and N atoms and their mobilities on the GaN growth surface, the rate of the Ga+N → GaN reaction, and the heat radiated to the target surface.

Since the drop in the deposition rate cannot be attributed to the densification of the film, it is concluded that the net rate of deposition of both Ga and N atoms is reduced at higher temperatures. One possible explanation is that adatoms are desorbed more rapidly at higher substrate temperatures. The rate at which atoms are incorporated into the growing film is

$$R_g = (R_{\text{inc}} - R_{\text{ref}}) - R_{\text{des}} \quad (1)$$

$$= R_{\text{ads}} - R_{\text{des}}, \quad (2)$$

where R_{inc} , R_{ref} , R_{des} , and R_{ads} are, respectively, the rates at which atoms are incident upon, reflected off, desorbed from, and adsorbed onto the substrate. The desorption rate from a layer of adsorbed atoms has the form

$$R_{\text{des}} = AB e^{-E_d/kT}, \quad (3)$$

where A is the fraction of the surface occupied by the layer, B is a frequency factor for desorption from the layer, and E_d is the energy required for an atom in the layer to overcome the surface forces.¹⁵ If it is assumed that the adsorption rate and the adatom coverage of the substrate do not change substantially with temperature, the (atomic) deposition rate can be written as

$$R_g = r_0(1 - d_0 e^{-E_d/kT}), \quad (4)$$

where r_0 is the deposition rate at low temperatures and $d_0 = AB/r_0$.

Since the density is essentially constant with the temperature, the spatial deposition rate should also take this form. Fitting Eq. (4) to the data of Fig. 1(a) gives values of $r_0 = 3.85$ nm/min, $d_0 = 20.4$, and $E_d = 0.22$ eV.

This fit suggests that the deposition rate should drop to zero above about 550 °C, but this is unlikely to occur since the surface coverage term A should be reduced for very high desorption rates. If the value of E_d is compared with values

in the literature, Al adatoms on NaCl and mica have adsorption energies of 0.6 and 0.9 eV, respectively.¹⁶ The values for Ga may be comparable because it is chemically similar and has a slightly lower bulk binding energy. However, the few values for Ga adsorbed onto GaN reported in the literature are considerably higher. Guha *et al.*¹⁷ reported a measured E_d value of 2.2 ± 0.2 eV for less than one monolayer of Ga adsorbed onto a GaN (001) surface. Adelmann *et al.*¹⁸ calculated from first principles that the adatom binding energies for single atoms and adatom islands on top of an adsorbed Ga bilayer were 2.52 and 2.41 eV, respectively. It is not possible to connect the E_d value extracted in the present study with other activation energies in the system, such as the cohesive energy of bulk Ga [2.8 eV (Ref. 19)] or the activation energy for the evaporation of GaN [3.6 eV (Ref. 20)]. One possibility, which has been overlooked, is that the temperature of the growth face, where adsorption/desorption occurs, may be substantially higher than the temperature of the substrate electrode or the substrate itself. This would effectively shift the plot of Fig. 1(a) to higher temperatures and thus increase the value of E_d considerably.

2. Pressure dependence

As the deposition pressure is increased [Fig. 1(b)], the deposition rate increases from 3.1 nm/min at 0.15 Pa, reaches a broad maximum of about 3.9 nm/min in the range 0.5–2.0 Pa, and then decreases again to 2.4 nm/min at 6.0 Pa. The pressure dependence of the deposition rate is likely to be a result of two competing processes. As the pressure is increased, there are more and more gas atoms/molecules available for ionization which should increase the number of ions attracted to the target and thus increase the deposition rate. However, at the same time, the mean free path of electrons in the plasma is reduced, lowering the average electron energy. This serves to reduce the probability of an atom being ionized by a collision, and thus the number of ions available for sputtering. The reduced mean free path also applies to the sputtered Ga species which means that less of the sputtered material reaches the substrate. The mean free path of unionized gas particles at 25 °C and 1.0 Pa is 7 mm, and the total target-substrate distance is around 50 mm. For these reasons, the deposition rate is maximized near 1 Pa.

3. Nitrogen fraction dependence

The deposition rate decreases approximately linearly with increasing N_2 fraction, from around 5.9 nm/min at 10% N_2 to around 2.1 nm/min at 65% N_2 [Fig. 1(c)]. Thereafter, it decreases more slowly but also linearly to around 1.5 nm/min at 100% N_2 . Dependencies of the deposition rate versus the reactive gas fraction showing an initial rapid decrease followed by a more gradual one have been observed in other material systems such as TaN,²¹ TiN,²² RuO₂,²³ and CrN/Cr₂N.²⁴ The rapid drop is usually ascribed to the formation of a layer of compound on the target. For sputtered GaN films, Ross and Rubin²⁵ observed an almost identical dependence to this experiment at 1.22 Pa, including a knee in the data at 65% N_2 . Lakshmi *et al.*⁶ also observed a simi-

lar dependence with a few data points and concluded that it was Ar which was mainly responsible for sputtering.

Heller²⁶ has modeled the effect on the sputtering rate of the surface oxide formation on the target under the assumption that the sputter yields of the reactive and sputtering gases are identical. At low partial pressures of the reactive gas, the target surface is clean and the sputtering rate is high (that of the metal in the sputtering gas). At a critical partial pressure P^* , which is a function of the particular sputtering system, total pressure, and rf power, a layer of compound forms on the target, dramatically reducing the sputtering rate because of the lower sputter yield. Hereafter, the deposition rate decays slowly to a limiting value which is that of a compound target.

According to this model there are two possibilities which depend on the precise forms of curves describing the reaction rate at the target surface and the sputtering rate, both as a function of compound thickness. They both start off with a Ga sputtering rate independent of the partial pressure of the reactive gas until a critical pressure at which the sputter rate equals the reaction rate and a compound forms on the target surface. Hereafter, the sputtering rate decreases slowly in an exponential like manner (type 1) or very rapidly (type 2) to the rate at which the nitride is sputtered.

Since the sputter yield changes with the sputtering ion, the sputtering rate of Ga in N_2 will be different from that in Ar. In addition, if GaN forms on the target, sputter yields in Ar and N_2 will once again be different. Thus, there are four different sputtering rates, namely, those of Ga in Ar, Ga in N_2 , GaN in Ar, and GaN in N_2 , denoted as $R_{Ga:Ar}$, $R_{Ga:N_2}$, $R_{GaN:Ar}$, and $R_{GaN:N_2}$, respectively. If it is assumed that the process taking place here is of type 2, with the decrease in sputtering rate approximating a step change, the deposition rate can be written as

$$R_{dep} = [xR_{Ga:N_2} + (1-x)R_{Ga:Ar}]u(x_0 - x) + [xR_{GaN:N_2} + (1-x)R_{GaN:Ar}]u(x - x_0), \quad (5)$$

where x is the fraction of N_2 in the sputtering gas, $u(x)$ is the Heaviside function, and x_0 is the nitrogen fraction at which the step change occurs. This fit to the data of Fig. 1(c) produces values of $R_{Ga:Ar}=6.5$, $R_{Ga:N_2}=-0.3$, $R_{GaN:Ar}=3.3$, and $R_{GaN:N_2}=1.5$ nm/min, and $x_0=0.64$. The value for $R_{Ga:N_2}$ is obviously incorrect, but it could be due to a change in the efficiency of ion formation, with increasing N_2 concentration affecting the slope of the first section of the curve. However, it does emphasize the dominance of Ga sputtering in Ar, when compared with Ga sputter rates in N_2 . It is also suspicious that $R_{Ga:N_2} < R_{GaN:N_2}$. However, $R_{Ga:Ar} > R_{GaN:Ar}$ and $R_{GaN:Ar} > R_{GaN:N_2}$, as expected. It has not been possible to find relative values of the sputter yields in the literature with which to compare these values.

Another possibility is that the curve is actually of type 1, but with x_0 shifted to very low N_2 concentrations and having an exponential-like dependence, but this function cannot be expressed analytically for fitting.

The model of Hrbek,²⁷ based on a reduction in sputtering rate as a result of increased adsorption (but not reaction) of the reactive gas at the target surface, provides a poor fit to

FIG. 2. AFM phase and SEM images of 1 μm films deposited at (a) -600 V, (b) standard conditions (room temperature, 2.0 Pa, 40% N_2 , and -800 V), (c) -1200 V, (d) 200 $^{\circ}\text{C}$, and (e) 20% N_2 . All scales are the same.

the data. In addition, a scum (presumably GaN) was often observed on the target when depositing at low sputter rates. However, this effect would increase the gradient of the low N_2 fraction part of the observed curve, which could explain the erroneous values of the earlier fit.

4. Target bias dependence

The deposition rate increases roughly quadratically with the target bias voltage from about 0.47 nm/min at -400 V to around 25 nm/min at -1800 V [Fig. 1(d)]. If it is assumed

TABLE I. The surface roughness and area smoothness calculated from the AFM amplitude deposition condition. R_q , R_a and A_n represent, the RMS roughness, the mean roughness and normalized surface area above a threshold value, respectively.

	-600 V	-800 V	-1200 V	200 $^{\circ}\text{C}$	20% N_2
R_q (nm)	9.3	6.8	2.8	6.3	2.8
R_a (nm)	7.4	5.1	2.2	4.6	2.2
A_n (%)	3.0	2.7	1.3	1.5	0.7

that the system used here is comparable to the dc sputtering process and that the ion sheath is predominantly collision-free, the Child-Langmuir law gives the ion current incident on the Ga target as proportional to $V^{3/2}$, where V , the voltage across the sheath, is taken to be approximately the same as the target bias voltage.¹⁴ The sputter yield as a function of ion energy can be divided into three regions.²⁸ The first, from the threshold to 100 eV, where there is a poor experimental reproducibility, will not be discussed. In the second, from 100 to 600 eV, the yield is approximately proportional to V , and in the third region, above 600 eV, it drops to $V^{1/2}$. If the dependencies of the ion current and the sputter yield are combined, the rates at which the material is removed from the target in the latter two regions are then proportional to $V^{5/2}$ and V^2 , respectively. Since both of these fit well to the experimental data, the film growth rate is assumed to be controlled primarily by the rate at which Ga is sputtered.

C. Crystal structure

The AFM phase and SEM images of selected 1 μm samples on Si are shown in Fig. 2 at the same magnification. The phase images were found to be especially useful for showing grain boundaries. The surface roughness and area calculated from the AFM amplitude plots are given in Table I. For the sample deposited at -600 V, crystallites are well defined and protrude from the substrate. The grain sizes are as large as 250 nm in diameter. At -800 V, the crystallites are smaller and more variable in size, and at -1200 V, the sample is very flat and the crystallites uniformly small. The rms roughness decreases from 9.3 nm for the -600 V sample to 2.8 nm for the -1200 V sample. This trend towards a reduction in the crystallite size and surface roughness is mirrored in 100 nm samples deposited every 200 V between -400 and -1400 V. However, the surface features are much smaller than for the 1 μm samples. Films may be more crystalline at low deposition biases because the deposition rates and the energies of most particles in the system are lower. Thus, adatoms can move about the surface for a longer time without being covered by incoming atoms, and there should be less damage to the growing crystallites by incoming particles.

The 1 μm sample deposited at 200 $^{\circ}\text{C}$ shows similar grain sizes to those of the room-temperature deposited sample, but there are what appear to be many fissures on the surface of each grain. SEM images of 100 nm films at 18 , 150 , 300 , and 450 $^{\circ}\text{C}$ appear to show a grain size increase as a function of temperature, but films are smoother than those deposited at low bias voltages. For a 20% N_2 fraction during

FIG. 3. Dark-field cross-sectional TEM image of 20% N_2 film showing a columnar morphology.

growth, the surface is as smooth as the -1200 V sample, but the $1\text{ }\mu\text{m}$ sample has the smallest normalized surface area of all the thick samples. At higher N_2 concentrations (60%, 80%, and 100%), the 100 nm film surface becomes increasingly featureless.

Although it was not possible to grow a $1\text{ }\mu\text{m}$ sample at 0.5 Pa because the sample delaminated completely during deposition, images of 100 nm samples deposited at 0.15 and 0.5 Pa show a surface too smooth to image properly. The greater mean free path of atoms at lower pressures means that particles hit the substrate with increased energy, possibly producing an increasingly stressed and disordered film. A 100 nm sample deposited at 6.0 Pa shows essentially the same surface morphology as that of the 2.0 Pa sample.

Cross-sectional TEM characterization showed that in most cases, the crystallites are columnar in shape, with the column width increasing towards the top surface of the film. This is in agreement with the trend observed using SEM. The presence of many spots forming discontinuous rings on the selected area diffraction (SAD) patterns showed that the films are polycrystalline although the degree of crystallinity differs. The relative spacing of the rings show that the material is predominantly wurtzite GaN.

The TEM samples exhibiting the greatest crystallinity are $1\text{ }\mu\text{m}$ thick, deposited at 20% N_2 and 200°C . They have large, clear grains which start right at the substrate-sample interface and reach up to 60 and 100 nm in diameter at the top surface. This value for the 200°C samples is smaller than that shown by the AFM phase image. The discrepancy may either be a result of the way in which the sample has been sectioned or it may mean that what appear to be single crystallites in the AFM image are, in fact, groups of crystallites. The SAD patterns close to the surface of the 20% N_2 film show an array of clear spots, which suggests that there are only a few large crystallites in the region of observation. For the 200°C sample, the SAD pattern shows bright continuous arcs which may indicate a gradual change in orientation within a crystallite or a range of crystallite orientations about a preferred orientation. The columnar grain structure of the 20% N_2 film is shown in Fig. 3, where the dark-field TEM image was obtained by selecting individual GaN reflections.

Thin films deposited at 450°C and 0.25 Pa are very disordered. The 450°C sample has crystallites of the order

FIG. 4. Relative elemental composition of 100 nm films.

of 5 nm, no obvious columnar growth, and a diffused SAD pattern. The 0.25 Pa sample is also extremely disordered, as shown by an even less well defined SAD pattern, but the high resolution TEM images do show lattice fringes and there are some column like illuminated areas in the dark-field images.

D. Chemical composition

The elemental composition of samples was obtained using EDX. For this analysis, the SEM accelerating voltage was lowered to 4 kV for the 100 nm samples to reduce the electron penetration depth such that the X-ray peak from the Si substrate was all but invisible. Thicker samples were measured at 10 kV. A calibration to prevent under-reporting of O and N concentrations was carried out on sapphire and high quality, metal-organic chemical-vapor deposition (MOCVD)-grown GaN.

The quartz shield surrounding the plasma was found to be essential in reducing the oxygen contamination of the films. Under standard deposition conditions, the O content of 500 nm thick films increased on removal of the shield from 3 to 26 at. %, irrespective of whether the target was presputtered. A possible reason is that the plasma is not contained without the shield, filling the entire deposition chamber. Thus, a contact with the plasma may release a steady supply of adsorbed gases such as water and oxygen, which are readily incorporated into the growing film. The relative atomic percentages of Ga, N, and O in the samples are plotted in Fig. 4. As a function of the substrate electrode temperature, the oxygen content increases monotonically from 3.2 at. % at room temperature to 9.7% at 375°C and 20.3% at 450°C . The ratio of Ga:N is essentially constant at around 1:1. As a function of pressure, there is a region in the range 0.25–2.0 Pa, where the O contamination changes only slightly from 2.8% to 3.3%. At lower and higher pressures, the O content increases. At 0.15 Pa, it is 4.4%, and at 4.0 and 6.0 Pa, 8.2% and 10.8%, respectively. As a function of the N_2 flow rate, the O concentration increases at both low and high flow rates. As the N_2 flow rate is increased, the O concentration in the film changes rapidly from 18.2 at. % at 10% N_2 to a shallow minimum at 40% N_2 , before increasing

FIG. 5. Elemental deposition rate obtained by multiplying the atomic fraction of a specific element by the deposition rate.

slowly to about 7 at. % at 100% N_2 . The N/Ga ratio increases from 0.68 at 10% N_2 to 1.18 at 100% N_2 . The value at 40% N_2 , with the O minimum, is 0.98. The high Ga concentration at low N_2 flow rates has often been measured or inferred in the literature.^{5,6,25}

The most dramatic change in the level of oxygen contamination is as a function of the target bias. At -400 V, this is about 30 at. % but decreases rapidly to around 3.2% at -800 V, after which it decreases very slightly to 2.6% at -1400 V. The N/Ga ratio is fairly constant, except at low biases where it decreases from 0.98 at -800 V to 0.82 at -400 V.

If the nitrogen in sections of the film were replaced with oxygen so as to form Ga_2O_3 , it would do so such that the relationship between the Ga, N, and O atomic percentages would be $d(Ga_{at. \%} - N_{at. \%})/dO_{at. \%} = 2/3$. However, this is not observed for these films. At high temperatures, there is no change in the Ga:N ratio and at high pressures, perhaps even a slight increase in the concentration of nitrogen relative to gallium. At low target biases, there is a slight reduction in the Ga:N ratio, but the change is only about 1/3 of the expected value. Thus, O does not simply replace N, nor is it incorporated as Ga_2O_3 .

If it is assumed that the atomic density (atoms/nm³) is approximately constant under all the deposition conditions, it is possible to obtain a sort of *elemental deposition rate* for each constituent element by multiplying the spatial deposition rate by the relative atomic fraction of the film. This allows the rate at which each individual element is incorporated into the growing film to be determined. The elemental deposition rates for Ga, N, and O are plotted in Fig. 5.

As a function of temperature, the O deposition rate increases from 0.12 to 0.26 nm/min, while the Ga and N rates decrease from 1.9 to 0.5 nm/min. This suggests that the increased O concentration at elevated temperatures is partially a result of the low Ga and N deposition rates which would allow a fixed absolute O incorporation rate to result in an

increased relative concentration in the deposited film. The increased absolute O incorporation rate is thought to be caused by an accelerated desorption of O_2 and H_2O off parts of the deposition chamber adjacent to the heater.

The O deposition rate is essentially constant at 0.12 nm/min for deposition pressures from 0.15–2.0 Pa, but jumps to around 0.27 nm/min for depositions at 4.0 and 6.0 Pa. At these higher pressures, a significant amount of arcing takes place between the target and the earth shield, possibly releasing additional H_2O and O_2 because of local heating. A reduction in the amount of available atomic N might increase the O incorporation, but this is unlikely because the N/Ga ratio increases slightly at higher pressures. Thus, the O incorporation rate is essentially constant where there is no arcing, and the reduction in the Ga deposition rate at high and low pressures increases the O contamination of the films. It appears that the increased energy of sputtered atoms reaching the substrate at lower pressures (because of fewer collisions) does not have the effect of removing adsorbed O atoms, as was thought to occur by Zembutsu and Kobayashi,⁷ where a negative substrate bias reduced the amount of O incorporation because of ion bombardment.

As the N_2 fraction in the deposition atmosphere is increased from 10% to 100%, the O concentration initially decreases from 18.2 at. % at 10% N_2 to 3.2 at. % at 40% N_2 . In the same range, the N concentration increases from 33.1 to 47.8 at. %. The relationship between the Ga, N, and O atomic percentages in this region is $d(Ga_{at. \%} - N_{at. \%})/dO_{at. \%} = 0.95$. Thus, it appears that the missing N atoms are replaced by O atoms. The O incorporation rate is decreased from 1.07 nm/min at 10% N_2 to 0.12 nm/min at 40% N_2 . This high incorporation rate at low N_2 ratios is ascribed to gettering of the available O in the deposition atmosphere in the absence of sufficient atomic N. At higher N_2 concentrations, the O concentration increases slowly, reaching around 7 at. % at 100% N_2 , but since the O incorporation rate is fairly constant in this region, it is likely that this increase is due to the decreased deposition rate.

As a function of the target bias voltage, the increase in the Ga and N deposition rate is more than ten times that of the O deposition rate. From -400 to -800 V, the absolute O incorporation rate is more or less constant, after which it increases slowly up to -1400 V. This is interpreted to mean that at medium to low target bias, the increase in relative O contamination with a reduction in bias voltage is due to the reduction in Ga and N deposition rates and a constant O incorporation rate. At higher bias, the relative oxygen contamination continues to decrease, but this is only because the absolute Ga and N incorporation rates increase at a much greater rate than the absolute O incorporation rate. The increase in the absolute O incorporation rate is ascribed to the increased energy of the plasma increasing desorption from the chamber walls.

The trends in the O/N ratio measured using electron-energy-loss spectroscopy (EELS) in the TEM agree with the trends reported here using EDX in the SEM. Oxygen contamination of GaN samples deposited by reactive sputtering has been reported a number of times in the literature with values of up to 5,²⁹ 9,³⁰ 15,³¹ and 20 at. %.⁷ In the one case

FIG. 6. Compressive biaxial stress in 100 nm films on Si as a function of (a) N₂:Ar flow ratios and (b) the negative target bias voltage.

where the H concentration was also measured,³¹ the H and O contamination levels were almost the same at 16 and 15 at. %, respectively. Although the source of H was ascribed to the contamination of the source gases, it is speculated that it could be due to the desorption of H₂O off the chamber walls.

E. Biaxial stress

The biaxial stress was measured in an earlier experiment, and as a function of the target bias and deposition nitrogen fraction, where the pressure was 1.85 Pa, the N₂ fraction is 33%, and the top electrode is floating. The values of the compressive biaxial stress are plotted in Fig. 6. There appears to be a fairly linear increase in biaxial stress from 1.2 GPa at 33% N₂ to 4.7 GPa at 75% N₂. This increase may be responsible for the delamination of films deposited at 60% N₂ and above. As the target bias is increased, the stress also increases from around 0.1 GPa at -400 V to 3.2 GPa at -1025 V. The reason for this may be the increased energy of sputtered atoms at higher target biases impacting on the growing film, or it may be because at the high deposition rates, there is insufficient time for incoming atoms to take up optimal positions in the film before they are covered with more materials. No delamination was observed at high biases for 100 nm films, possibly because the increased energy of particles hitting the target causes some substrate-film mixing or relaxation at high fluxes. In the current experiment, it is also thought that films deposited at low pressures have an increased biaxial stress because the larger mean free path means that particles have higher energies. When a 1 μ m thick film was grown at 0.5 Pa, the film delaminated during deposition, whereas the others, at high N₂ flow rates, usually delaminated slowly afterwards.

F. Optical properties

1. General

Fairly typical absorption spectra of films deposited at different temperatures are plotted in Fig. 7(a) and the absorption coefficient squared in 7(b). At low photon energies, up to around 2.4–3.4 eV, the dominant feature is interference because of internal reflections within the films. The fundamental absorption at the band edge takes place at higher photon energies for the samples deposited at the higher temperatures. The increased O concentration shown by EDX may be responsible since the band gap of β -Ga₂O₃ is in the range 4.7–4.9 eV,^{32–34} as compared with the 3.4 eV of GaN.

FIG. 7. Total absorbance of the film and substrate (a) and absorption coefficient squared (b) at various substrate electrode deposition temperatures.

The curves of Fig. 7(b) are remarkably similar to those observed by Butcher *et al.*³⁵ for an increased O contamination in GaN deposited by remote-plasma enhanced CVD. For the current experiment, plots for decreasing target bias voltages, which have increasing O contamination levels, exhibit the same trend. This adds weight to the view that O contamination has a major effect on the optical absorption spectrum close to the band edge.

2. Band gaps

The optical band gaps are plotted versus the deposition parameters in Fig. 8. As a function of the substrate electrode temperature, the band gaps increase from 3.02 eV at room temperature to 3.60 eV at 450 °C. The rate of change is low to around 200 °C and increases thereafter. The increase is primarily ascribed to a shift of absorption to higher photon energies because of an increase in the O content of the films. Some of the initial increase may be partially due to the improved crystallinity and reduced band tailing because of the increased thermal energy allowing Ga and N atoms to migrate over the surface during growth and take up more optimal positions in the growing film.

As a function of the N₂ fraction, the band gap initially increases very rapidly from 2.49 eV at 10% N₂ to a plateau above 25% N₂ at around 3.07 eV and then increases again above 70% N₂. The initial band gap increase corresponds to a visible change from dark brown or black to a slightly yellowish color in transmission. In view of the EDX results, this is ascribed to a reduction in the amount of excess Ga in the

FIG. 8. Optical band gaps for 100 nm films.

FIG. 9. Urbach tail energies for 100 nm films.

film. However, in this region, N atoms seem to be replaced by O atoms, but there may not be enough oxygen present to react with all the Ga. It is not clear what is responsible for the band gap increase at higher N_2 fractions.

The correlation between the optical band gap value and the level of O contamination is most clearly demonstrated as a function of the target bias. The band gap values are very high at low target biases, reaching more than 4.00 eV at -400 V, but are essentially constant at around 3.03 eV for -600 V and above.

3. Urbach tail energy

Films which are thick enough for color in transmission to be determined by the absorption of the films rather than by interference are yellowish, except where there is a significant O contamination. This absorption is visible below the band edge as band tailing into the blue part of the spectrum.

The Urbach tail energy E_0 , which is often used to quantify the band tailing and thus the disorder in the material, is plotted in Fig. 9. As a function of the substrate electrode temperature, the value varies around 150 meV up to 300 °C, possibly decreasing slightly, before increasing rapidly to 470 meV at 375 °C and to 840 meV at 450 °C. Slack *et al.*³⁶ have suggested that the Urbach tail could be caused by O impurities. Figure 7(a) shows how the spectral features of films deposited at higher temperatures and O content tend to be smeared out.

At low N_2 flow rates, the values are large and are likely to be a result of excess Ga, giving rise to significant absorption right into the band gap. There appears to be a shallow minimum at around 40% N_2 , after which the values increase again at higher N_2 flow rates. The increase may be related to the decrease in Ga and to the increase in O. A plot of E_0 versus the negative target bias voltage also shows a minimum in the range of -600 to -800 V. Above -1400 V, the values decrease again. The large values at low target biases may once again be related to the smearing of the band edge by O contamination. However, the minimum may reflect an improved crystallization due to the low target bias, but without the gross O contamination of the very low biases.

In regions with more than 5% O contamination, the band gap exhibits similar trends to those of the Urbach tail energy. The only exception to this is at low N_2 flow rates where the films are Ga rich and the increased oxygenation is only as a response to the decrease in the availability of nitrogen. Because of the way in which the band gaps are inferred from the optical absorption curves, a decrease in the Urbach tail energy should be accompanied by an increase in the band gap because a reduction in tail states should sharpen the band edge. Thus, large values of E_0 can mostly be ascribed to an excess of oxygen rather than to any real trend in terms of improvement in the crystal structure. The minima in the plots of E_0 as functions of the N_2 flow rate and target bias voltage coincide with the standard deposition conditions. This may indicate that these conditions are close to optimal for the given setup.

4. Refractive index

The trends in the refractive indices are essentially opposite to those of the optical band gaps. This is expected because of the Kramers-Kronig relationship between the wavelength dependence of the real and imaginary parts of the refractive index, n and k . Films having a large O content show very low values of refractive index, and the measurement seems to be a fairly sensitive indicator of this. The refractive index of the disordered β -Ga₂O₃ is 1.89 at 632.8 nm.³² Under standard deposition conditions, the refractive index of the GaN is 2.46, just short of the highest reliable value of 2.47 at 75 °C. The lowest values were obtained at 450 °C (2.03), 90% N_2 (2.23), and -400 V (1.73–2.04). For the severely oxygenated samples deposited without the quartz shield, refractive index values were in the range 1.91–2.03 for 30%–70% N_2 and only reached 2.2 at a target bias of -1400 V.

IV. CONCLUSIONS

The deposition rates of GaN films formed by reactive sputtering vary over a wide range, from 0.47 to 25 nm/min, depending on the deposition conditions. As a function of temperature, pressure, N_2 fraction, and target bias, the deposition rates are considered to be controlled, respectively, by thermally activated desorption from the substrate, changes in the mean free path and concentration of gas particles, differences between the sputter yields of Ga and GaN in Ar and N_2 , and changes in the ion current and sputter yields.

The films are polycrystalline and generally columnar, with the grain size increasing with film thickness. The most crystalline films were grown at midrange temperatures, low N_2 concentrations, and low target biases, and the most disordered at low pressures. The latter two cases suggest that decreasing the energy of particles incident on the film during deposition results in a more ordered film. The biaxial stress is compressive and shows an increasing trend with the N_2 concentration and target bias.

The stoichiometry, the oxygen contamination in particular, has a major effect on the optical properties of the films, masking any effect of the degree of the structural disorder. Oxygen contamination tends to smear out the band edges and

shift the band gap values to higher energies. This increases the Urbach tail energies and decreases the refractive index values. Except as a function of N_2 in the deposition atmosphere, the N/Ga ratio is more or less constant. The absolute oxygen incorporation rate changes very little, but it is the relative film deposition rate which determines the final oxygen concentration. At low N_2 concentrations, Ga getters oxygen from the deposition atmosphere in the absence of sufficient atomic nitrogen. The excess Ga makes the films opaque to the naked eye, and this is reflected as a decrease in the band gaps and an increase in the Urbach tail energy.

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