ABSTRACT

Title of dissertation:	REAL-TIME IN-SITU CHEMICAL SENSING IN AlGaN/GaN METAL-ORGANIC CHEMICAL VAPOR DEPOSITION PROCESSES FOR ADVANCED PROCESS CONTROL
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Gallium nitride and its alloys promise to be key materials for future semiconductor devices aimed at high frequency, high power electronic applications. However, manufacturing for such high performance products is challenged by reproducibility and material quality constraints that are notably more stringent than those required for optoelectronic applications. To meet this challenge, in-situ mass spectrometry was implemented as a real-time process- and wafer-state metrology tool in AlGaN/GaN/AlN metal-organic chemical vapor deposition processes on semi-insulating SiC substrate wafers. Dynamic chemical sensing through the process cycle, carried out downstream from the wafer, revealed generation of methane and ethane reaction byproducts, as well as other residual gas species. Real-time metrics were derived based on the chemical signals to predict/control material quality and thickness of critical layers within the heterostructure in real time during growth, and corresponding metrologies were used for real-time advanced process control. Using the methane/ethane ratio, GaN epilayer crystal quality was predicted in real time to 2 - 5% precision, which was verified by post-process x-ray diffraction. Moreover, the same real-time metric predicted material quality as indicated by post-process photoluminescence band-edge intensities to ~5% precision. The methane/ethane ratio has a fundamental significance in terms of the intrinsic chemistry in that the two byproducts are believed to reflect two parallel reaction pathways leading to GaN-based material growth, namely the gas phase adduct formation route and the surface route for direct precursor decomposition, respectively. The fact that lower methane/ethane ratios consistently yield better material quality suggests that the surface pathway is preferred for high quality GaN growth. In addition, a metric based on methane and ethane signals integrated through the AlGaN growth period (~1 min or less) enabled prediction of the cap layer thickness (~20 nm) to within ~1% precision, which was verified by postprocess x-ray reflectance.

These types of real-time advanced process control activities in terms of fault detection and management, course correction, and pre-growth contamination control have made significant contributions to the GaN-based semiconductor development and manufacturing at Northrop Grumman Electronics Systems in terms of improved material quality, yield, and consequent cost reduction, and they are now in routine use.

REAL-TIME IN-SITU CHEMICAL SENSING IN AlGaN/GaN METAL-ORGANIC CHEMICAL VAPOR DEPOSITION PROCESSES FOR ADVANCED PROCESS CONTROL

by

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Soon Cho

2004

DEDICATION

To my mother, father, and sister whom I love the most.

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configurations and process conditions are described in Table 4.1, and AlGaN thickness map is also shown in Fig. 2.5. (data from Aumer)

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- FIG. 4.2 Run-to-run variation in product AlGaN cap layer thickness as determined by XRR. Shown are the data from all HEMT heterostructure growth runs performed on semi-insulating SiC substrates during an arbitrary period in the year 2003. Considering that typical thickness process windows are in the range of 20 25 nm, these runs could imply a yield as low as ~31%.
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 $(\Delta \sim 17 \text{ nm})$. The real-time film thickness metric based on methane and ethane signals measured by mass spec exhibited a strong linear correlation (3.9% precision) to the actual film thickness grown, as measured by post-process XRR.

- FIG. 4.4 AlGaN cap layer thickness metrology within the thickness range of 74 ~6 nm. The real-time film thickness metric based on methane and ethane signals measured by mass spec exhibited a strong linear correlation (1.2% precision) to the actual film thickness grown, as measured by post-process XRR.
- FIG. 5.1 Real-time prediction of GaN PL band-edge intensity during growth 81 based on in-situ mass spec measurement of methane/ethane byproducts ratio (precision 4.8%). The four runs shown here correspond to the same four runs presented in Ch. 3 on crystal quality prediction, where it was shown that the same methane/ethane ratio metric predicts GaN epilayer crystal quality to 3.5% verified by post-process XRD. Moreover, the correlation is such that by going to lower methane/ethane ratio we improve material quality as seen in both XRD and PL.
- **FIG. 5.2** Correlation of the gas phase residual H₂O level within the reactor during GaN epitaxy to the GaN PL band-edge intensity measured post-process. Better quality material (as seen in higher band-edge intensity) was obtained when the residual H₂O level was lower.
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- **FIG. 5.5** Correlation of the gas phase residual impurity level, measured at amu 55, within the pre-growth reactor to the GaN PL band-edge intensity measured post-process. Better quality material (as seen in higher band-edge intensity) was obtained with *higher* (not lower) impurity level detected prior to growth with the correlation accurate to 10% here. Further study is required to determine the exact identity of the unknown specie at amu 55 and its effect on the process.

- **FIG. 5.6** Correlation of the gas phase residual O₂ level within the pre-growth 86 reactor to the GaN PL deep-level intensity measured post-process. Better quality material (as seen in lower deep-level intensity) was obtained when the pre-growth residual O₂ level was lower with the correlation accurate to 19% here. Although the correlation here is less precise compared to the case of PL band-edge intensity, this offers an important means to predict and possibly control GaN deep-level concurrent with the band-edge intensity, because the two parameters put together are critical as a measure of GaN material quality.
- FIG. 6.1 An example of real-time fault detection based on clear chemical signatures for process and equipment faults which potentially lead to unacceptable product quality. (a) Desorption of H₂O vapor from the unconditioned walls of a brand new liner as soon as the temperature ramp begins, followed by desorption of impurity coating from a dirty susceptor in the form of N₂ during the high temperature purge.
 (b) Such impurity evolutions were not observed with a well conditioned liner and a clean susceptor. These kinds of real-time indications as in (a) clearly correlated to unacceptable material quality by PL, and they indicated a need for measures to correct the root cause, such as through extended pre-growth contamination control and replacement of corresponding tool parts (e.g., susceptor).
- **FIG. 6.2** An example of real-time detection of an equipment excursion in the 92 middle of process that led to unacceptable material quality. Failure of an NH₃ MFC was immediately detected by the mass spec during GaN epilayer growth from the real-time signatures indicating large disturbances in the NH₃ concentration within the reactor. Segment A indicates a manual test where the isolation valve between the mass spec and the reactor was closed for a period of $\sim 2 \text{ min}$. Stable NH₃ signal (still remaining high due to the trapped volume within the sampling inlet of the sensor) during this period as well as the time scale for each sensing scan (10.353 s) confirmed that the disturbances were real physical effects and not an electrical noise. Segments B and C indicate a series of MFC flow variation tests where the set point for the MFC flow rate was altered between a high value (80% for B) and a low value (40% for C). Results of the test indicate that the MFC failed to perform properly for low flow rate set point conditions. The MFC in question was replaced immediately and both the sensor signals as well as the future product materials themselves indicated that the fault was successfully resolved.

- FIG. 6.3 Mass spec sensing during a run where the reaction byproduct (CH_4 93 and C_2H_6) levels were significantly lower than the usual. This was correlated to the little growth of product film seen post-process, which led to examination of a limited number of possible sources for the fault. Once the root cause was identified to be the untimely precursor source depletion, the precursor source bottle was immediately replaced. The segment labeled "EM off" indicates a test where the mass spec electron multiplier was turned off for ~2 min and then turned back on to confirm that it was functioning properly.
- FIG. 8.1 Schematic representation of an experimental setup for spatially104 resolved local sensing by the same mass spec system used to achieve metrology and control at the downstream location (see Fig. 2.1). A long quartz capillary, together with two motion devices, allows sensing at specific locations between the showerhead and the susceptor, contributing to better understanding of the intrinsic process chemistry occurring near the actual growth region.

LIST OF ABBREVIATIONS

2DEG	two-dimensional electron gas
μm	micrometers
A	Ampere
ALD	atomic layer deposition
AlGaN	aluminum gallium nitride
AIN	aluminum nitride
amu	atomic mass unit
APC	advanced process control
Ch(s).	chapter(s)
cm	centimeters
CVD	chemical vapor deposition
DMGA	dimethylgallium adduct
DOE	design of experiment
Fig(s)., FIG.	figure(s)
FDC	fault detection and classification
FTIR	Fourier transform infrared spectroscopy
FWHM	full-width at half-maximum height
g	grams
GaN	gallium nitride
h	hours
H_2	hydrogen
HEMT	high electron mobility transistor
HF	hydrogen fluoride
i.d.	inner diameter
in.	inches
LED	light emitting diode
m	meters
mass spec	mass spectrometry
mg	milligrams
min	minutes
MOCVD	metal-organic chemical vapor deposition
N	nitrogen
N ₂	nitrogen gas
NH ₃	ammonia
nm	nanometers
0. a .	outer diameter
DEE	overall equipment efficiency
	personal computer
	photofulminescence
КГ	ratio frequency
S	stondard oubia continutors nor minute
Soc(s)	standard cubic-centimeters per minute
sec(s).	silicon carbida
SIC	SHICOH CALUIDE

SIMS	secondary ion mass spectrometry
SIT	static induction transistor
slm	standard liters per minute
SOD	sea of data
Т.	temperature
ТМА	trimethylaluminum
TMG	trimethylgallium
ULSI	ultra large scale integration
W	tungsten
WF ₆	tungsten hexafluoride
XRD	x-ray diffraction
XRR	x-ray reflectance

Chapter 1 Introduction and previous work

1.1 Advanced process control

Advanced process control (APC) has become a critical enabling technology for the semiconductor manufacturing industry, enhancing productivity and profitability. The two primary thrusts of APC, namely *course correction* and *fault management*, have different goals and attributes.¹⁻⁷ (See Fig. 1.1) Course correction is intended to adjust process parameters so that product quality is maintained in spite of short-term variability and long-term drift in process and equipment behavior, while fault management is aimed at identifying equipment problems that would cause such variability and repairing them in an optimal time frame.

Real-time fault detection, based on *in-situ sensors*, has already become a widely accepted practice in semiconductor manufacturing to monitor real-time performance of tools in order to minimize the number of misprocessed wafers. By immediate identification and response to known process and equipment faults, this first component of fault management provides substantial value to manufacturing productivity, and it has been widely implemented using in-situ sensors, particularly using mass spectrometry (mass spec). Other aspects of fault management are more challenging and will thus require more sophisticated approaches, including more general *fault classification* (where sensor signals do not readily distinguish the cause of faults), and *fault prognosis* for optimal scheduling of tool maintenance actions.

Course correction has been widely adopted for manufacturing in the form of *run-torun control* (or wafer-to wafer control). Guided mainly by *in-line metrology* [e.g., x-ray

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reflectance (XRR), x-ray fluorescence, four-point probe]⁸ rather than by in-situ sensors, run-to-run control can rely on well developed metrology tools that are not typically integrated into the process equipment, and it provides a powerful strategy to compensate for long-term systematic process drift using both *feedback* and *feedforward control*. In contrast, APC course correction based on in-situ sensors is only beginning to emerge as a significant component of overall APC strategy in the industry,⁹ because it requires in-situ metrology with sufficient precision to enable subtle quantitative process adjustments. On the other hand, if adequate in-situ metrology were available, it would present a major benefit not only as an alternative to in-line metrology for run-to-run course correction, but particularly for *real-time* course correction. In-situ metrology could then be employed to compensate for random short-term variability that occurs within a process step, as well as for long-term systematic process drift, and it would complete a more powerful APC strategy that includes tool-level real-time control (course correction and fault detection) in a larger context of hierarchical APC.¹ (See Fig. 1.2)

In principle, in-situ sensors can provide the metrology needed for either run-to-run or real-time course correction. In-situ sensors have been utilized in run-to-run control (e.g., in chemical mechanical polish and lithography processes) and in selected applications for real-time control (e.g., for interferometric etch end-point control and rapid thermal processing). However, in-situ sensors have seen only limited application for material deposition processes, particularly for mainstream Si technology applications such as chemical vapor deposition (CVD), despite the potential benefits. While several in-situ real-time sensing techniques have been investigated for process monitoring, including quadrupole mass spec,¹⁰⁻¹⁹ acoustic sensing,²⁰⁻²³ UV spectroscopy,^{23,24} and Fourier

transform infrared spectroscopy (FTIR),^{25,26} a primary limitation in employing such techniques for real-time manufacturing course correction has been the lack of demonstrated metrology precision sufficient to deliver real value in manufacturing.

1.2 Previous work on W CVD metrology and control

Our research group has been developing such real-time in situ sensing methodologies for CVD process diagnostics, metrology, and APC course correction, using quadrupole mass spec and other chemical sensors.^{10-17,20} In recent years (2000 – 2001), my investigations have focused on W CVD processes with the primary goal of improving the metrology to a sufficient precision – taken as about 1% – that it would be viable for CVD thickness control in high-volume manufacturing, as either run-to-run or real-time control.^{10-13,20} This target is consistent with metrology requirements in the *International Technology Roadmap for Semiconductors* (ITRS): 4% 3 σ for gate dielectric and 10% 3 σ for barrier layer at 4 – 7 nm.⁷ The current section of the dissertation reports the advances in the precision of real-time, in-situ CVD thickness metrology that clearly exceed the 1% target we have been seeking. These achievements have been published elsewhere²⁷⁻³⁰ and only a summary of results are discussed here.

1.2.1 Low-pressure W CVD

As a background, prior to achieving our goal of <1% metrology precision in 10 Torr W CVD processes, others in our group had explored lower pressure W CVD processes using both H_2/WF_6 (H_2 reduction)^{11-13,20} and SiH₄/WF₆ (SiH₄ reduction)¹⁰ chemistries. In

the case of H_2 reduction at 0.5 Torr, in agreement with the widely accepted reaction mechanism

$$3H_2 + WF_6 \rightleftharpoons 6HF_{(g)} + W_{(s)}, \qquad (1.1)^{31}$$

we observed H₂ reactant depletion and volatile HF byproduct generation using in-situ downstream mass spec. Time-integration of these mass spec signals, together with postprocess ex-situ film weight measurement, provided a working metrology model such that real-time mass spec signals could be used to predict in real time the average W film thickness deposited on the wafer. In this case, the metrology result based on HF byproduct generation signal yielded an average uncertainty on the order of 7%.¹¹ This was similar to other results obtained by acoustic sensor measurements carried out for the same processes.²⁰ The precision of both mass-spec- and acoustic-sensor-based metrologies was limited primarily by the low conversion (or utilization) rate of the reactants (~3%) achieved for this process chemistry, temperature regime, and lowpressure (sub-Torr) operation of the reactor. Our analysis concluded that the metrology was limited by the conversion rate of reactants (since it was based on byproduct generation or reactant depletion) and that higher reactant conversion rates (~30%, as commonly experienced in manufacturing applications such as blanket W CVD at >50 -100 Torr) would significantly improve the sensor signal-to-noise ratio and thus the metrology accuracy. An additional drawback resulting from the low conversion rate of the sub-Torr process was that an additional mass spec measurement was necessary (with the wafer at room temperature and process gases flowing) in order to calibrate and compensate for a background signal associated with reactant adsorption and reaction on

chamber walls;¹¹ needless to say, any such background calibration step would be absolutely unacceptable in manufacturing.

In order to improve the metrology precision and demonstrate its suitability for APC, we then investigated the SiH₄ reduction process, knowing that SiH₄ is a more efficient reducing agent, as follows:

$$3SiH_4 + 2WF_6 \rightleftharpoons 6H_{2(g)} + 2W_{(s)} + 3SiF_{4(g)} \tag{1.2}^{32}$$

This led to a reasonable conversion rate (~20%) and a thickness metrology precision of order 1 - 2%, and we demonstrated real-time end-point control of film thickness to within 3% of target in the face of 10% open-loop wafer-to-wafer thickness variation.¹⁰

1.2.2 High-pressure W CVD

We then modified the W CVD reactor (Ulvac ERA1000 production scale cluster tool) to enable higher pressures (up to ~100 Torr total pressure) in the range typically employed in W CVD manufacturing processes and reconfigured our mass spec sampling system accordingly, which are shown schematically in Fig. 1.3. Metrology results were obtained for the H_2 /WF₆ processes at a higher pressure of 10 Torr, under three sets of conditions: (1) a nominally fixed process condition, (2) intentionally introduced run-to-run process temperature drift, and (3) intentionally introduced run-to-run deposition time variation. The results demonstrated quantitative thickness metrology with precision of 1% or better. Details of the work are described in separate publications²⁷ and only a summary of results are presented here.

Metrology development

In-situ mass spec sensing of the 10 Torr W CVD process provided us with dynamic, real-time gas phase chemical signals as a function of the process cycle. Figure 1.4 shows characteristic ion current signals from the H₂ and WF₆ reactants, HF byproduct, N₂ purge gas, as well as other species used to monitor reactor cleanliness (H₂O, WOF₄) and parasitic reactions on the quartz showerhead (SiF₄, SiHF₃). Partial pressures of these species exhibit strong time dependence through the process cycle, including background levels before and after the single-wafer process, N₂ purge cycles before (segment A) and after (segment C) the process, and dynamics within the process itself (segment B). In particular, during the process, the reactant gases (H₂ and WF₆) and the reaction byproduct species exhibit different dynamics. This is primarily a consequence of the reactor residence time, which determines the rate at which reaction byproduct generation and reactant depletion attain steady state.

Among the various chemical signals, the characteristic signals indicating H_2 and WF_6 reactant depletion and HF byproduct generation were considered good candidates for thickness metrology based on the known reaction mechanism and stoichiometry described by Eq. (1.1). We found that the HF byproduct generation signal at 20 amu (atomic mass unit), integrated through the entire deposition cycle, provided us with the best metrology accuracy. Figure 1.5 shows the HF byproduct signal, which we integrated through the process cycle to obtain a thickness metrology.

Run-to-run process drift and metrology under fixed process conditions

A batch of ten wafers was processed under identical nominal process conditions at 10 Torr, 400 °C, for a fixed deposition time of 640 s. Despite the fixed process condition specified by the tool set points, an average of 1.18% run-to-run process drift was manifested in the post-process film weight measurement, as seen in Fig. 1.6. The actual variation in film weight was 3.0 mg on average, which corresponds to 20 nm in terms of film thickness as estimated assuming the bulk density of W to be 19.35 g/cm³. Such runto-run process drifts can have significant impact on manufacturing yield and have been a strong motivation for industry adoption of run-to-run control as a prime component of APC. The drift appears to include random as well as systematic components, with the deposited film weight exhibiting a systematic drift of 0.40% for each successive wafer. We attribute this run-to-run drift to increased W nucleation on the quartz showerhead and chamber walls for each successive run leading to easier W deposition at those non-wafer surfaces, as discussed further in the next set of experiments.

Despite the unintentional run-to-run drift present in the process, real-time, in-situ metrology based on time-integration of the HF byproduct signal reveals the drift directly and is quantitatively correlated with the post-process film thickness measurements, as seen in Fig. 1.7. A linear regression fit was made through the ten-wafer run, and the average difference between the actual film weight measurement and the predicted value from the regression model provided us with a metric for quantitatively determining our metrology accuracy. We called this metric the average uncertainty, which for this batch of ten wafers was found to be 0.56% over the total range of film weight variation of 10.2 mg (or 67 nm in terms of estimated film thickness).

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Intentionally introduced run-to-run process drifts and metrologies

In order to understand the effects of equipment and process drifts, and to evaluate the robustness of the metrology precision, we carried out further batch deposition runs with intentionally introduced run-to-run process drifts. In the first case, a systematic temperature drift (total of 60 °C) was gradually introduced over 18 wafers under otherwise fixed conditions. Effects of the temperature drift on the process were clearly observed in terms of the HF byproduct generation and WF₆ reactant depletion behaviors as shown in Fig. 1.8. The corresponding metrology result indicates that despite the large dynamic range of film thickness variation (~4X or $1.4 \mu m$) due to the intentional process drift, the real-time in-situ measurement provides an appreciable precision at around any given local range (~0.5%) as shown in Fig. 1.9.

In another case, an intentional run-to-run variation in deposition time (~3X over 10 wafers) was introduced under otherwise fixed conditions, in order to explore its use as our control variable for real-time film thickness control. Here again, we explored a much larger variation in process metrics (i.e., film thickness variation of 1.5 μ m; see Fig. 1.10) than would be a target for APC course correction in manufacturing. Nevertheless, the real-time in-situ thickness metrology derived from the mass spec signal was capable of precision on the order of 1% or better (depending on the regression fit model), indicating value for APC course correction in either run-to-run or real-time end-point control (see Fig. 1.11 for real-time end-point control strategy). These results based on mass spec sensor were shown to be consistent with those from acoustic²⁹ and FTIR³⁰ sensors used concurrently with the mass spec for the same set of W CVD processes.

I have been closely involved in these sensor-based metrology development and control efforts in W CVD as a prototype, especially primarily involved in the latter two cases (i.e., closed-loop end-point control of SiH₄/WF₆ processes¹⁰ and metrology development in 10 Torr H₂/WF₆ processes²⁷⁻³⁰), and the results have been presented at numerous international symposiums^{28,30,33-35} and journal publications.^{10,27,29} Readers are referred to them for details of the works.

1.3 AlGaN/GaN for advanced electronic applications

In recent years, gallium-nitride (GaN)-based materials and its alloys have distinguished themselves to be key materials for future semiconductor devices aimed at high frequency and high power electronic operation.³⁶⁻³⁸ Unlike the rapidly expanding applications for GaN technology in optoelectronics (e.g., light emitting diodes), such high performance electronic applications place greater demands on the material quality which is needed for desired device performance. However, despite the potential of these materials, currently the level of control and reproducibility in these processes are no where near that achieved in the silicon-based semiconductor manufacturing, because of the complexity of the process chemistries involved, the earlier stage of the technology's evolution, and the consequent absence of emphasis on APC.

Although GaN metal-organic chemical vapor deposition (MOCVD) processes have been investigated in some depth, its intrinsic chemistry is still debated.³⁹⁻⁶⁶ Typically, MOCVD of GaN and AlGaN hetero-epitaxial films are grown at high temperatures (e.g., up to 1100 °C) using large concentrations of H₂ (carrier) and NH₃ (N source), and relatively small concentrations of metal (group III) precursors, trimethylgallium (TMG)

or trimethylaluminum (TMA). The variety of active species and reaction pathways accessible at such elevated temperatures give rise to complex parasitic reactions both in the gas phase and on the surface, as shown in Fig. 1.12.⁶⁷ Reactions that occur in the gas phase are expected to form complex adduct species which further decompose to form a trimer specie before finally decomposing to form GaN on the hot wafer surface. This adduct pathway releases several molecules of CH₄ (methane) as the reaction byproduct. On the other hand, the metal-organic precursor can decompose directly on the hot wafer surface to grow GaN, releasing primarily C₂H₆ (ethane) as its reaction byproduct. Different groups have modeled³⁹⁻⁵⁰ and observed the growth process using a variety of insitu monitoring techniques, including mass spec,⁵¹⁻⁶⁰ FTIR,⁶⁰⁻⁶³ laser light scattering,^{63,64} ellipsometry,⁶⁵ and laser reflectometry,⁶⁶ However, controversy continues over the exact chemistry in play. Furthermore, we note that most mechanistic studies of GaN have addressed temperature regimes notably below 800 °C (e.g., room T. – 800 °C for Kuech et. al.^{40-45,52,53} and room T. – 300 °C for Creighton et. al.^{39,51,63,64}). In contrast, the present work focuses on the regime above 1000 °C, where electronic applications of GaN are focused.

Despite the growth chemistry that is not well understood, it is possible to achieve significant reproducibility in metrologies based on appropriate in-situ sensors, sufficient to drive their use in APC, since this does not require mechanistic understanding of the operative chemistry. Such sensors deliver real-time process-state information for *fault detection and classification* (FDC) of the process and equipment (e.g., ensuring tool cleanliness with low background impurity levels and monitoring of process for real-time signatures of tool failures). In addition, it has been demonstrated that the wafer-state

information derived from such real-time sensor signals can be used to provide precision metrology and real-time control of the growth process itself to achieve desired postprocess targets as in the case of W CVD discussed in the previous section. These kinds of FDC and course correction activities based on in-situ sensors have become prominent in the silicon ULSI (ultra large scale integration) industry, which is now witnessing a widespread adoption of APC.¹⁻⁹

1.4 Research objectives, approach, and significance

Our research group has been an active contributor in various aspects of APC, especially in the use of real-time in-situ chemical sensors for both FDC and course correction.^{1,10-17,20,27-30,33-35} In view of the relevant challenges currently facing the development of GaN-based processes for manufacturing in electronic applications, I have applied similar APC approaches based on our past experience in Si-based processes (e.g., W CVD discussed in Sec. 1.2) in hopes of achieving process reproducibility sufficient for manufacturing. I have employed in-situ mass spec in AlGaN/GaN/AlN MOCVD processes to grow high electron mobility transistor (HEMT) heterostructures on semiinsulating SiC for high frequency/power electronic devices. In this dissertation, I report the application of real-time, in-situ chemical sensing to film thickness control, intrinsic material quality prediction, fault detection, and contaminant control in GaN-based systems.

In particular, the use of real-time, in-situ chemical sensing for film thickness control had been demonstrated in the prototype case of W CVD²⁷ as discussed already in Sec. 1.2. However, the achievements demonstrated here for the case of AlGaN thickness control

represents a crucial step forward from a number of different perspectives. First of all, it is demonstrated here that the same methodology can be extended into the nanoscale regime with similarly high precision (~1%) in metrology. For instance, the AlGaN cap layer (~20 nm) here is orders of magnitude thinner than the blanket W layer (>1 μ m) in the previous W CVD case. This is important because the semiconductor ULSI industry is now dealing with various kinds of ultra thin (nanoscale) layers, such as barrier layers or gate dielectrics by CVD or ALD (atomic layer deposition) – a challenging requirement for the precision of in-situ sensors.⁷ Not a traditional thickness monitoring sensor, mass spec metrology demonstrated here achieves nm - even atomic - precision. Secondly, the extremely low level of byproduct signal intensities, in part due to their low partial pressures in the system, posed a considerable challenge for their use as real-time waferstate metrics requiring high precision as discussed earlier. Nevertheless, this is typical in most MOCVD-based thin film growth processes, which is gaining increasing number of applications in the semiconductor manufacturing (e.g., Cu MOCVD for interconnects), and here the challenge is successfully overcome by implementing special experimental measures as described in detail within the dissertation.

In addition, one single aspect of the dissertation work that distinguishes itself from all of the rest to date has to do with the demonstration of real-time intrinsic material quality prediction and its application to control. I report here development of a working real-time metric (i.e., the methane/ethane byproducts ratio based on the intrinsic process chemistry model) for accurately predicting the crystal quality of the product GaN epilayer during growth (precision $\sim 2 - 5\%$), along with the associated metrology models appropriate under various process and equipment conditions. Implications of the findings are far-

reaching in terms of real-time fault detection and management and course correction for real-time material quality control, systematic designing of process conditions and equipment configurations for material quality optimization, and improved insight into the GaN intrinsic process chemistry, all of which are discussed in detail within the dissertation.

Furthermore, there are other important pieces of results based on the sensing of GaNbased processes that led to practical implementation, such as the real-time GaN photoluminescence (PL) qualities prediction and the associated pre-growth contamination control. All of these achievements are considered extremely significant from the points of view of both advancement of semiconductor manufacturing science and technology in the long run, as well as immediate benefits to the industry (in this case, Northrop Grumman Electronic Systems). In particular, the latter point is distinguished considering the enormous cost savings (e.g., the current average cost of ~\$3000 for a 2 in. semiinsulating SiC wafer and the absence of reproducibility in the subsequent GaN-based thin film processes using the wafer as the substrate).

Advanced Process Control (APC)



FIG. 1.1. Schematic representation of the major components of APC. The work described in the dissertation focuses on real-time control as well as real-time fault detection.

APC Hierarchy



FIG. 1.2. Schematic representation of the hierarchy of control occurring in a fab. The work described in the dissertation focuses on providing real-time APC, with both real-time course correction and real-time fault detection components, as a more powerful regulatory controller at the unit process level, thus complementing the existing run-to-run course correction and fault management based on in-line metrology at the higher level as well as regulatory controllers at the tool level.



FIG. 1.3. Schematic representation of the 300 amu in-situ quadrupole mass spec gas sampling system (Inficon model CIS2^{TM}) attached to the Ulvac ERA1000 cluster tool reactor for H₂/WF₆ W CVD processes at 10 Torr. Not drawn to scale.


FIG. 1.4. In-situ gas phase chemical signals from mass spec, indicative of the dynamic gas composition downstream of the reactor as a function of process steps. The mass spec current signals were acquired in real time together with the equipment-state signals from the tool control. Segment A indicates the pre-process N_2 purge period. Segment B indicates the deposition cycle, which includes the reactor filling period and the raw process time at 10 Torr. Segment C indicates the reactor pump-down and the final N_2 purge period. The substrate heater temperature was nominally maintained at 390 °C at all times for this particular run through segments A, B, and C.



FIG. 1.5. In-situ HF byproduct generation signal obtained in real time during the deposition cycle. Metrology signal was obtained by integrating the HF signal over the entire deposition period (segment B), which includes the reactor filling period as well as the raw process time at 10 Torr. This particular example is taken from the same run as in Fig. 1.4.



FIG. 1.6. A batch of 10 wafers processed (1 wafer per run) under identical nominal process condition at 10 Torr, 400 °C for a fixed deposition time of 640 s. A run-to-run systematic drift as well as random variations in the processes were manifested in the post-process W film weight measurement with an average run-to-run variation of 1.18%.



FIG. 1.7. Film thickness metrology model based on in-situ time-integrated HF signal and ex-situ W film weight measurement for the 10 wafers processed under nominally fixed process condition as shown in Fig. 1.6. A 1st-order linear regression fit yielded an average uncertainty of 0.56% within the corresponding range of film weight variation of 10.2 mg (or 67 nm in terms of estimated film thickness).



FIG. 1.8. A batch of 18 wafers processed (1 wafer per run) with an intentionally introduced run-to-run drift in wafer temperature for every 2 wafers. Run-to-run changes in magnitude as well as shape of the HF byproduct generation and the WF_6 reactant depletion signals were observed as shown. Wafer (or run) numbers are indicated above each corresponding HF signal.



FIG. 1.9. Film thickness metrology model based on in-situ time-integrated HF signal and ex-situ W film weight measurement for the 18 wafers processed under run-to-run temperature drift as shown in Fig. 1.8. Note that the 1st wafer of the batch was excluded for metrology purposes due to the 1st wafer effect as discussed in other publications. For metrology purposes, two separate local regions were distinguishable at different temperature ranges, both of which displayed an average uncertainty on the order of 0.5% from linear regression fits as shown. The corresponding range of film weight variation (or estimated film thickness) was 87.9 mg (or 578 nm) for wafers #2-#10 and 129.3 mg (or 850 nm) for wafers #9-#18.



FIG. 1.10. Film thickness metrology model based on in-situ time-integrated HF signal and ex-situ W film weight measurement for 10 wafers processed at 390 °C and 10 Torr for 5 different deposition times (2 wafers/runs for each deposition time). A 1st-order linear regression fit yielded an average uncertainty of 1.19% within the corresponding range of film weight variation of 231.9 mg (or 1526 nm in terms of estimated film thickness).



Strategy for Real-Time APC (Thickness)

FIG. 1.11. Strategy for real-time end-point process control for film thickness.



FIG. 1.12. Schematic representation of the proposed reaction pathways leading to GaNbased materials growth by MOCVD. The gas phase reaction pathway leads to complex adduct formation and reactions that result in CH₄ as its characteristic byproduct, whereas the surface reaction pathway is formed by the direct decomposition of the metal-organic precursor on the hot wafer surface that produces C_2H_6 as its characteristic reaction byproduct. It is assumed that both pathways exist in parallel in a typical GaN growth process discussed in this dissertation and their relative contributions can be measured by the methane/ethane byproducts ratio during growth. (modeling and figure by Parikh and Adomaitis)

Chapter 2 AlGaN/GaN growth, sensing, and characterization

2.1 Metal-organic chemical vapor deposition of AlGaN/GaN

Experiments were carried out within a water-cooled quartz-wall reactor (custom designed) as shown schematically in Fig. 2.1. The reactor is ~13 L in volume and includes a quartz liner inside a double quartz furnace wall. The system uses a commercial gas delivery system supplied by EMF. Reactants (NH₃, TMA, and TMG) with the carrier gas (H₂) were delivered through two quartz delivery tubes fused to a custom designed quartz showerhead. In particular, the metal-organic precursors (TMA and TMG) and NH₃ were kept separated in their respective delivery tubes until they reached the showerhead, at which point they intermixed uniformly within the showerhead before being delivered to the wafer region below. Single wafer substrate (2 in. diam semi-insulating SiC from Cree) was placed on the SiC-coated graphite susceptor. The susceptor was inductively heated at 10 kHz to provide heating for the film growth to occur on the wafer. The residual process gases were continuously pumped away through the exhaust lines located at both ends of the reactor, connected to a common rotary vane pump.

The typical process sequence used to grow GaN-based HEMT heterostructures in our experiments is described in Table 2.1. It began with 30 - 60 min of pre-growth room temperature reactor purge. During this period, the reactor (including the showerhead, liner, and susceptor) was purged with 25 slm of H₂ at room temperature without intentional heating of the susceptor. Once the reactor has undergone sufficiently long purge to achieve acceptable low levels of background impurities (H₂O, O₂, etc.) as monitored by the mass spec, heating of the susceptor was initiated. During this step,

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temperature was ramped at ~1 °C/min until it reached the desired set point for growth (typically 1000 – 1200 °C as measured via a sapphire light pipe directed at the bottom of the susceptor). Once the temperature reached its final set point, it was maintained for an additional 5 min to outgas background impurities from both the susceptor and the liner in the presence of the H₂ purge gas. During this high temperature reactor purge, progress in removing impurities was monitored in real time using the same mass spec used for the HEMT growth sensing. In particular, the background impurity levels measured by the mass spec were noted at the end of this high temperature reactor purge step for correlation to post-process material characterization, as discussed in Ch. 5. Once an acceptable growth environment was prepared through these pre-growth reactor purge steps, the actual HEMT heterostructure growth sequence was initiated, which is separately described in detail in the following section.

Following the growth of the HEMT heterostructure at 50 Torr, the residual process gases were pumped away and the wafer was cooled under NH_3 at 300 Torr to prevent GaN decomposition. This was followed by further cooling under H_2 and cycle purge of the reactor to complete the process and remove the wafer for post-process characterizations.

Further descriptions of the process conditions and the tool are provided in Sec. 3.1.

2.2 High electron mobility transistor heterostructure growth

The sequence and conditions of the growth process were defined by the design of the GaN-based HEMT heterostructure required for our advanced microwave electronics application. Usually, it consisted of three layers grown on the as-received semi-insulating

(resistivity >1E5 Ω -cm) 4H-SiC(0001) substrates (2 in. diam) as shown in Fig. 2.2. (1) First, ~100 nm thick AlN(0001) layer was grown to provide nucleation sites for the subsequent GaN growth and to improve the lattice mismatch ($\sim 3.3\%$) between the SiC(0001) substrate and the GaN(0001) epilayer. The thickness of the AlN layer must be carefully optimized in order to avoid GaN layer cracking (due to overly thick AlN) or poor GaN crystal quality (due to overly thin AlN). (2) Secondly, ~1 µm thick GaN epilayer was grown on the AlN nucleation layer. The bulk of the GaN epilayer is expected to be electrically insulating, while the two-dimensional electron gas (2DEG) near the interface of the GaN epilayer with the AlGaN cap layer forms the transistor's channel for carrier transport. In order to achieve such requirements, a number of important material parameters must be carefully optimized including the epilayer thickness, crystal quality, and impurity content, because they affect the 2DEG concentration, background carrier concentration, their mobilities, etc. (3) Finally, 20 - 25nm AlGaN cap layer was grown on the GaN epilayer to complete the heterostructure. The AlGaN cap layer composition (usually target 30 - 35% Al for band gap energy of ~4.0 eV) as well as the thickness (usually target 20 - 25 nm) must be precisely optimized and controlled for optimum electrical performance of the final device. For instance, the cap layer composition is critical for determining the device breakdown characteristics (suffers with increasing Al content) and the 2DEG concentration (diminished with decreasing Al content), whereas the cap layer thickness (d) directly affects the final device performance in terms of transconductance (g_m) and the frequency of unit current gain (f_T) as follows:

$$f_T \propto g_m \propto \frac{1}{d} \tag{2.1}^{68,69}$$

In addition, too thick of a cap layer results in increased pinch-off voltage, while too thin of a cap layer results in diminished 2DEG. The growth of all three layers occurred as sequential steps within the same process, and the in-situ mass spec was used to monitor the progress in real time through the entire process cycle.

2.3 Real-time in-situ chemical sensing by mass spectrometry

2.3.1 Sensor sampling system design and operation

The mass spec sampling system used is shown schematically as part of Fig. 2.1. The process and residual gases were sampled directly from the reactor downstream via a 1/16-in.-o.d. x 0.010-in.-i.d. x 20-cm-long stainless steel capillary, which resulted in a pressure drop from the process pressure of 50 Torr down to ~1 Torr behind the capillary. Most of this gas was then pumped away by a bypass differential pumping to the foreline of the diaphragm pump (backing pump for the mass spec's turbomolecular pump), leaving only a small fraction of the gas to enter a 20- μ m-i.d. orifice into the closed ion source region of the mass spec (Inficon model CPMTM, 200 amu quadrupole mass spec).

By using an appropriately sized capillary-orifice combination for the gas conductance network, the sampled gas pressure was reduced from the viscous flow regime (50 Torr) to the molecular flow regime (~1 Torr). The bypass differential pumping technique enabled us to actively withdraw gases from the process through the sampling system. Both of these sampling techniques, as well as the location of the sampling capillary (i.e., within the main gas flow downstream to the growth reaction), were critical in achieving adequate response time in process sensing.

The W filament current in the closed ion source was kept at 200 μ A, while the electron energy was maintained at 40 eV. This provided adequate sensitivity and minimum parasitic reactions within the closed ion source region. Electron multiplier detection was used at an acceleration voltage between 775 V and 1250 V in order to enhance and maintain the signal-to-noise ratio run-to-run.

2.3.2 Downstream process sensing

In-situ mass spec sensing of the 50 Torr MOCVD growth process as described above provided dynamic, real-time gas phase chemical signals as a function of the process cycle. Figure 2.3 shows characteristic ion current signals from H_2 (carrier gas), NH₃ (column V precursor), N₂ (fragmentation product from NH₃), H₂O (background impurity), CH₄ (reaction byproduct), C₂H₆ (reaction byproduct), C (background impurity), and O₂ (background impurity). Partial pressures for these species, reflected in the ion currents, exhibit strong time dependence throughout the entire process cycle, including the initial and final stages of the AIN, GaN, and AlGaN growth steps. This is primarily a consequence of the reactor residence time, which determines the rate at which reaction byproduct generation and reactant depletion attain steady state whenever there is a change in process chemistry (e.g., going from GaN growth to AlGaN ternary alloy growth). Virtually no column III precursors (TMA and TMG) were detectable in their original chemical form at the downstream location. This is primarily attributed to the close to complete decomposition and utilization at the extremely high growth temperature near the wafer and showerhead regions. Note also that for the reaction byproducts methane and ethane, mass peaks at 13 and 26 amu's were used, instead of 16 and 30

amu's as one might expect. These values were chosen from components in the fragmentation patterns of the parent species to minimize ambiguity where mass fragments from multiple sources overlap. Specifically, this was an attempt to avoid large overlap in spectrum for the species present in the system including NH₃ (fragmentation pattern at 17, 16, 15, and 14 amu's) and N₂ (fragmentation pattern at 28 and 14 amu's; and parasitic ion-molecule reactions to produce N_x-H_y species at 15, 16, 29, and 30 amu's). Small overlaps (< 8%) may have existed between methane and ethane signals knowing that additional methane can be formed inside mass spec ion source as a fragment of the original ethane from the MOCVD reaction. However, with the fixed operating condition for the mass spec, the minute overlap would be consistent run-to-run and therefore negligible for the purpose of our analyses described in this dissertation.

2.4 Post-process ex-situ material characterizations

2.4.1 X-ray diffraction

The samples grown on SiC substrates as described in the preceding sections were examined using a number of post-process characterization techniques, including x-ray diffraction (XRD), XRR, and PL – and less frequently sheet resistance, Hall effect measurement, and secondary ion mass spectrometry (SIMS). In particular, the XRD was performed using a Bede D1TM system equipped with microsource capability for higher spatial resolution. Rocking curves were obtained at 81 points on an equally-spaced rectangular grid over the 2 in. wafer. Full-width at half-maximum height (FWHM) of the individual rocking curves were obtained and averaged to provide a measure of the

average crystal quality of the GaN epilayer. For set A runs, FWHM's were measured for both the on-axis (002) symmetric and off-axis (102) glancing exit reflections. The on-axis reflection (most commonly reported) alone is considered to be insufficient as a metric for GaN crystal quality because it is not affected by edge dislocations (i.e., the material can have large density of edge dislocations and still produce a narrow (002) peak.). However, it was found over the course of many runs that the presence of the two types of defects (edge and screw dislocations) were in general correlated (i.e., found together), and the off-axis (102) reflection therefore did not provide any additional information to that from the on-axis (002) reflection. Also, in an effort to improve our throughput, the number of points analyzed across the wafer was reduced to nine beginning in set C runs in Ch. 3.

2.4.2 X-ray reflectance

The same x-ray machine (Bede $D1^{TM}$ system) was also used to measure the thickness of the AlGaN cap layer (~20 nm), where the separation of interference fringes in the XRR mode was used by the automated software to deduce the film thickness at each point as follows:

$$\Delta \theta = \frac{\lambda \gamma_g}{t \sin(2\theta_B)} \tag{2.2}^{70}$$

where $\Delta \theta$ is the interference fringe separation, λ is the x-ray wavelength, γ_g is the cosine of the angle between the diffracted beam and the inward-going normal to the sample surface, *t* is the layer thickness, and θ_B is the Bragg angle for diffraction. Measurements were made at 42 points on a polar coordinate grid over the 2 in. wafer to generate a wafer-wide contour fit map for the AlGaN thickness and a corresponding histogram (area weighted) as shown in Fig. 2.5. The average value from the histogram was then used as a measure of the average AlGaN thickness reported in this dissertation.

2.4.3 Photoluminescence

The PL characterization (by Accent RPM2000TM compound semiconductor PL system) provided multiple important semiconductor material quality metrics in a relatively timely manner. A 266 nm pulsed laser was incident on the sample and a UV-enhanced CCD camera captured the spectrum. The r- θ stage allowed the entire wafer mapping in min's at 30 pts/s and a resolution of 1 mm. The spectral scan mode provided information on the characteristic peaks at both the band-edge (364.6 nm) and deep-level (550.1 nm) for the GaN layer, where the band-edge intensity reflects the ratio of radiative to non-radiative recombination, and the deep-level (or yellow luminescence) is related to defects, impurities, and mid-gap/surface states within the material. Additional information such as the FWHM for crystal quality and the alloy composition for the AlGaN cap layer were obtained from the same measurement technique, and the white light spectrum mode provided the GaN epilayer thickness from the interference fringe separation. Here, we used the band-edge [Fig. 2.6(a)] and deep-level [Fig. 2.6(b)] intensities averaged over the 2 in. wafer as measures of average material quality, and the similarly averaged epilayer thickness [Fig. 2.6(c)] to deduce the average growth rate.

2.5 Sensor integration for real-time advanced process control

Although all of the metrology development works discussed in this dissertation were possible without a complete tool-sensor *real-time* signal integration, it is essential for

implementation of *real-time* process control (both FDC and course correction) based on the metrologies developed here. Figure 2.7 shows a schematic representation of real-time information flow among the various entities in our GaN APC setup. The GaN MOCVD system is depicted in the upper left corner with its pumping and in-situ sensing of the reactor. The chemical sensor (i.e., mass spec) is controlled, and its information is gathered and displayed, in real time by Inficon TWareTM, a Microsoft WindowsTM-based commercial software that comes with the sensor. Typically, the sensor data is then saved in .SOD format (native format for TWareTM-based data files), which can be reopened using the same software or used to generate reports in .TXT format for further postprocess analyses and metrology development.

However, in order to enable *real-time* APC we constructed an additional set up, which includes a stand-alone National Instruments LabVIEWTM-based program that executes process control and fault detection in real time. This program (custom programmed by Cho and Janiak) resides on the same PC platform with TWareTM and acquires the relevant chemical sensor data in real time via Microsoft DDETM-based communication with TWareTM. DDETM (which stands for Dynamic Data Exchange) is a communication protocol that allows applications in the WindowsTM environment to exchange data and instructions between each other by establishing a client (e.g., our LabVIEWTM-based custom program) and server (e.g., TWareTM) relationship.

The LabVIEWTM program also acquires the relevant process gas flow information in real time from sensors installed on the MOCVD system. We used Mykrolis IPS-122 indicating pressure switches installed on the TMA, TMG, and NH₃ gas pneumatic valves, at a location immediately prior to entering the reactor itself. They provided 0/13.5 VDC

signals (based on the individual gas valve's closed/open status) to the LabVIEWTM program via a digital data acquisition board (Measurement Computing PCI-PDIS08). This provided information about which process step (i.e., pre-growth, AlN, GaN, or AlGaN) was currently in progress because different process steps require different process gases flowing into the reactor. Knowing where we are in terms of the process steps is important because it allows us to initiate and terminate computation of different real-time metrics at the exact timing and sequence (e.g., the cap layer thickness metric based on time-integration of the methane and ethane byproduct signals for the AlGaN growth step – see Sec. 4.1).

Finally, real-time process control is achieved by the LabVIEWTM program alerting the process engineer of its real-time decisions pertaining to the process- and wafer-states – for example, the process engineer terminates the flow of metal-organic precursors by manually proceeding to the next step in the process recipe, when the desired AlGaN thickness target is reached according to the real-time metric based on time-integration of the methane and ethane byproduct signals, as described in Sec. 4.1. However, closed-loop control based on the chemical sensor is yet to be completed due to difficulties imposed by the complexity of the MOCVD tool control system by EMF. Meanwhile, real-time viewing of the process- and wafer-state information on the LabVIEWTM program screen is considered sufficient in practice for our research scale growth system (Fig. 2.8). Nevertheless, there is an on-going collaboration with an MOCVD tool vendor for these kinds of control automation issues for our next generation production scale system to be installed in early 2005.

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Step#	Description	Duration	Pressure	Temperature	Gases on
1	room T. reactor purge	30 – 60 min	50 Torr	room T.	H_2
2	T. ramp-up	20 min	50 Torr	heating	H ₂
3	high T. reactor purge	5 min	50 Torr	at growth T.	H ₂
4	AlN growth	~15 min	50 Torr	at growth T.	H ₂ , NH ₃ , TMA
5	GaN growth	60 – 90 min	50 Torr	at growth T.	H ₂ , NH ₃ , TMG
7	AlGaN growth	1 – 3 min	50 Torr	at growth T.	H ₂ , NH ₃ , TMA, TMG
8	cooling with NH ₃	1 min	pump down (~45 Torr)	cooling	H ₂ , NH ₃
9	cooling with NH ₃	12 min	300 Torr	cooling	H_2 , NH_3
10	cooling with H ₂	15 min	300 Torr	cooling	H ₂
11	cycle purge	5 min 20 s	$5 \leftrightarrow 450 \text{ Torr}$	room T.	H ₂

TABLE 2.1. Typical MOCVD process sequence used to grow the GaN-based HEMT heterostructure discussed in the dissertation.



FIG. 2.1. Schematic representation of the 200 amu in-situ quadrupole mass spec gas sampling system (Inficon CPMTM) attached to the downstream of the quartz wall reactor system for the GaN-based MOCVD processes discussed in this dissertation.



FIG. 2.2. Schematic representation of a HEMT based on AlGaN/GaN/AlN/SiC heterostructure as grown by the MOCVD processes discussed in this dissertation. Not drawn to scale.



FIG. 2.3. In-situ gas phase chemical signals from mass spec, indicative of the dynamic gas composition downstream of the reactor as a function of process steps. The mass spec current signals were acquired in real time through the entire HEMT growth process. Shown here is an example taken from run G262, for which the equipment configurations and process conditions are described in Table 3.2.

G262 GaN (002) FWHM



FIG 2.4. An XRD wafer map of GaN (002) rocking curve peak FWHM. Rocking curves were obtained at 81 points on an equally-spaced rectangular grid over the 2 in. wafer. The FWHM of the individual rocking curves were obtained and averaged to provide a measure of the average crystal quality of the GaN epilayer. This example is taken from run G262, for which the process sensing information is shown in Fig. 2.3, and the equipment configurations and process conditions are described in Table 3.2. (data from Aumer)



AlGaN Thickness Map of G380 Wafer



FIG. 2.5. An XRR thickness map and histogram. Measurements were made at 42 points on a polar coordinate grid over the 2 in. wafer to generate (**a**) a wafer-wide contour fit map for the AlGaN cap layer thickness and (**b**) the corresponding histogram. The average value from the histogram was then used as a measure of the average AlGaN thickness reported in this dissertation. Note that this is an area-weighted average value. This example is taken from run G380, for which the equipment configurations and process conditions are described in Table 4.1. (data from Aumer)

(b)



FIG. 2.6. Examples of PL wafer maps showing (a) GaN band-edge peak intensity, (b) GaN deep-level peak intensity, and (c) GaN epilayer thickness. A 266 nm pulsed laser was incident on the sample and a UV-enhanced CCD camera captured the spectrum. The r- θ stage allowed the entire wafer mapping in min's at 30 pts/s and a resolution of 1 mm. Here we used the band-edge (364.6 nm) and deep-level (550.1 nm) intensities averaged over the 2 in. wafer as measures of average material quality, and the similarly averaged epilayer thickness to deduce the average growth rate. These examples are taken from run G380, for which the equipment configurations and process conditions are described in Table 4.1, and AlGaN thickness map is also shown in Fig. 2.5. (data from Aumer)



FIG. 2.7. A schematic representation of real-time information flow among the various entities in our GaN APC setup. A complete tool-sensor *real-time* signal integration is essential for implementation of *real-time* process control (both fault detection and course correction) based on the metrologies developed in this dissertation.



FIG. 2.8. Screenshot of the user interface of the LabVIEWTM-based custom program for real-time process control and fault detection. Elements of the relevant metrology models are input by the process engineer and the program automatically compares the metrics based on the current process sensing to the models to make real-time decisions for the process engineer.

Chapter 3 Real-time prediction and control of GaN epilayer crystal quality

3.1 AlGaN/GaN growth design of experiments

Three sets of runs were performed for the results discussed in this chapter. Each set was performed using significantly different tool configurations, particularly the showerhead-to-susceptor spacing and the showerhead design, as discussed in more detail at the end of the current section. For simplicity, we will denote these tool configurations by sets "A", "B", and "C" here. For all three sets, AlGaN/GaN/AlN HEMT heterostructures were grown on 2 in. semi-insulating SiC substrates as discussed already in the previous chapter. The individual HEMT heterostructures were grown under varying process conditions (TMG flows, growth temperature, growth duration, etc.) and using different equipment configurations (showerhead, liner, etc.) as described in Tables 3.1 - 3.3.

Typically, the TMG flow rate and the growth temperature were varied while the total pressure, carrier gas and NH₃ gas flow rates were maintained constant run-to-run. The process temperature set point (as measured via a sapphire light pipe directed at the bottom of the susceptor) was intentionally varied, and the actual temperature was confirmed by an independent optical pyrometer aimed at one side of the susceptor, which is reported in Tables 3.1 - 3.3. In addition to the two types of direct temperature measurements, other indirect means to infer the actual process temperature were also employed, including measurement of the cooling water temperature exiting the reactor and the utilized RF power output.

The showerheads were made of quartz and custom-designed by Adomaitis et. al. through a physically based model describing heat transfer and gas transport through the showerhead.⁷¹ For example, showerheads "F" (used for sets A and B runs) and "G" (used for set C runs) differed markedly in their hole pattern, size, and distribution. Both the showerhead and the innermost liner were removed from the reactor after each run. Showerheads were cleaned in ultrasonic KOH solution bath run-to-run, while the liners were used for ~3 runs without cleaning. On average, a showerhead could be used for ~10 runs before being replaced due to the effect of the showerhead surface roughening on film growth uniformity. Finally, the showerhead-to-susceptor spacing was intentionally varied by the use of 0.25 in. longer susceptor legs for sets B and C compared to set A.

3.2 Sensor-based real-time metric development

Because methane and ethane are clearly the byproducts of the growth reaction of our interest, it is expected that they contain the wafer-state information indicative of deposition on the wafer, as well as the process-state information normally expected. It has already been clearly demonstrated in the past that these kinds of in-situ sensor-based signals do indeed correlate to the wafer-state in real time, in some cases with high quantitative precision that allows precision metrology²⁷ and subsequent control¹⁰ of the wafer-state (e.g., film thickness deposited). Moreover, in this case, assuming that each of the two byproducts come from different reaction pathways to grow the GaN-based material on the wafer (see Fig. 1.12), methane/ethane ratio can be thought of as a measure of the relative contribution of each pathway for any given growth process. With this in mind, the methane/ethane ratio can be directly monitored in real time as shown in Fig. 3.1.

Averaging the values obtained through the entire GaN growth period provides the average methane/ethane ratio metric of our interest:

$$\frac{\int S(CH_4)dt}{\int S(C_2H_6)dt}$$
(3.1)

Next, we show how this sensor-based metric can be used to predict the product crystal quality in real time and the corresponding metrology results we have obtained in our three sets of GaN growth runs.

3.3 Real-time prediction of GaN crystal quality and metrology

Largely due to the variation in process condition, the resulting material qualities exhibited run-to-run variability. In particular, run-to-run variation in GaN epilayer crystal quality for set A runs is shown in Fig. 3.2 in terms of the XRD rocking curve FWHM. As discussed in the preceding sections, distortion of the on-axis (002) reflection is considered to be due to screw dislocations, whereas the off-axis (102) reflection is affected by both screw and edge dislocations. However, both types of measurement exhibited similar trends of run-to-run variation on the order of 29 arcsec or 11 - 12%.

Despite such unintentional variation in product crystal quality, we have found it can be successfully predicted in real time during growth using the methane/ethane ratio metric as discussed in the preceding section. Figure 3.3 shows the correlation between real-time methane/ethane ratio during growth and crystal quality as measured by postprocess XRD characterization. Linear fit to the data indicates that the correlation to the on-axis (002) reflection is accurate to within 12 arcsec or 5.1% average uncertainty, and similarly the off-axis (102) reflection to within 12 arcsec or 4.9% average uncertainty. The same results are also tabulated in Table 3.4 along with the GaN epilayer thickness information, which is calculated based on the PL interference fringe separation in the white light spectrum as discussed in Sec. 2.4.3. In general, thickness and growth rate correlate to the resulting crystal quality of the epitaxial films in such a way that larger thickness and lower growth rate are expected to produce better crystal quality epitaxial films. However, the PL thickness information along with the average growth rate deduced from the thickness showed that our metrology models based on the methane/ethane ratio are independent of the growth rate and film thickness within the range explored.

Finally, we note that a minimal measurement error was contributed by the high resolution XRD as described in Sec. 2.4.1. Although no specific numbers could be obtained, it is expected to be significantly less than the 2 - 5% precision of the in-situ metrology models presented in this chapter.

3.4 Effect of changes in tool configurations

In addition to establishing a working metrology model for the set A runs as discussed above, we have also observed similar correlations (between methane/ethane ratio and crystal quality) using two significantly different tool configurations. In particular, we have explored (1) smaller vertical spacing between the showerhead and susceptor in sets B and C; (2) significantly different showerhead design in terms of its hole pattern, size, and distribution in set C.

First of all, the use of 0.25 in. longer susceptor legs for sets B and C runs resulted in relatively smaller vertical spacing between the showerhead and susceptor compared to set A. In particular, for set B similar process/tool conditions were used (including same

showerhead design) as in set A, so the only significant difference was the showerhead-tosusceptor spacing. In order to determine whether the same correlation would hold under such a different tool configuration as in set B, we monitored the methane/ethane ratio in real time and compared it to post-process crystal quality measurement as before. The results indicated that indeed the same correlation held true for the (002) reflection as seen in Fig. 3.4 and Table 3.5 (i.e., smaller methane/ethane ratio predicting better GaN crystal quality). Moreover, the correlation was accurate to within 5 arcsec or 2.0% according to the linear metrology model.

Secondly, in set C runs showerheads with completely different design (in terms of its hole pattern, size, and distribution) were utilized while keeping the same showerhead-to-susceptor spacing as in set B. Results of the real-time methane/ethane ratio correlated to post-process crystal quality measurement on the (002) reflection are plotted in Fig. 3.5 and tabulated in Table 3.6. Again, the same correlation held true for set C as well with precision on the order of 9 arcsec or 3.5% based on the linear metrology model.

Overall results indicate that small methane/ethane byproduct ratios identify better GaN epilayer crystal quality, with the corresponding metrology accurate to within 2 - 5%average uncertainty, depending on the tool configuration and the associated model for the different set of runs. This is confirmed by the correlation between the real-time methane/ethane ratio measured by in-situ chemical sensing of the reaction byproducts and the post-process GaN crystal quality measured by XRD for changes in process conditions at a fixed tool configuration. In turn, significant changes in tool configuration (i.e., the showerhead design and the spacing between showerhead and susceptor) necessitated a change in the model, but for each tool configuration a model gave a strong correlation between mass spec metrology and crystal quality.

3.5 Elements that determine metrology and control model

The metrology models developed above, based on correlation between real-time mass spec measurements of methane/ethane ratios and post-process GaN crystal quality characterization by XRD, display substantial validity (a few %) in the presence of modest intentional changes made in run-to-run process condition within each set as seen in Tables 3.1 - 3.3. There also existed numerous non-intentional factors within each individual set in terms of the growth conditions, which ultimately contributed to the run-to-run material quality variation but was still well described by the model.

For example, as the showerhead aged run-to-run, its surface roughened (i.e., area increased) due to bonding of materials during process and their removal during post-process KOH cleaning; this affected the depletion of precursor within the showerhead and therefore the film growth uniformity on the wafer. The use of different liners brought about slight variation in the showerhead-to-susceptor spacing because the showerhead was designed to rest on the horizontal crossbar built into the liner itself, whose position unintentionally varied to within the glass fabrication error of <0.125 in. This would have affected the temperature and chemistry within the showerhead positioned directly above the hot susceptor. In fact, variability observed in the run-to-run sensing data motivated a reactor design modification to eliminate the liner as a source of such variability for future runs. These types of influences on the gas phase chemistry during process are expected to manifest in terms of the final material quality such as the crystal quality. Finally,

conditions of the underlying AlN nucleation layer and SiC substrate were inconsistent run to run, which would have influenced the GaN epilayer grown over them. This has been proven through our routine XRD wafer mapping, where the original defects within the SiC substrate could indeed translate to undesirable defects within the AlN and GaN layers grown over them, unless steps were taken during the AlN layer growth to minimize their effect.

Despite all of these intentional and non-intentional sources of variability that lead to run-to-run variations in the process environment and resulting material quality, results show that a single model developed using one tool configuration provides quantitative predictability of crystal quality over a reasonable range of process conditions. However, the models indicate strong dependence on the tool configuration parameters such as the showerhead-to-susceptor spacing and the showerhead design. These points are illustrated clearly in Fig. 3.6. The model relating mass spec predictors of crystal quality and actual XRD measures of crystal quality changes significantly with changes in tool configuration. However, once the tool configuration is fixed, the associated model transforms the mass spec measurement into an effective predictor of material quality (to a few % precision).

3.6 Prognosis for applications

Even though the XRD rocking curve data are only supposed to reflect a qualitative or semi-quantitative measure of a material's crystal quality, such a correlation as seen here between real-time wafer-state metric based on sensors and post-process product quality can be extremely useful from the viewpoints of both development and manufacturing. The methane/ethane ratio offers an extremely useful metric that can be quickly utilized to identify process conditions that optimize product crystal quality. With GaN technologies still in development, this is extremely useful. For instance, a single design of experiment (DOE), containing multiple short period (~30 s) GaN growth steps within to explore a wide range of process conditions (in terms of temperature, pressure, flow rates, gas composition, etc.), may be performed on a semi-insulating SiC with a usual AIN nucleation layer. The average methane/ethane ratio resulting from each individual GaN growth step can be monitored and recorded in real time. Knowing that lower methane/ethane ratio will have a greater chance of producing better GaN crystal quality, an optimal window of process condition can be selected and employed in subsequent real HEMT heterostructure growth runs. This offers a systematic methodology to improve/tune GaN-based processes with drastically reduced turn-around time and cost.

Furthermore, since the metric is based on real-time in-situ metrology, it can be exploited for real-time control of the MOCVD growth process in the context of APC. In one scenario, the mass spec signature can be employed for fault detection, identifying in real-time wafers for which material quality may be degraded and triggering corrective actions ranging from more in-depth characterization to debugging and repair of equipment. Such FDC approaches have already been widely adopted in the Si ULSI industry as discussed in Sec. 1.1.

In another scenario, the real-time mass spec predictors of material quality may be employed for course correction. If an appropriate process parameter, or a set of parameters, can be identified which can improve material quality as reflected in the methane/ethane ratio, then drift in this ratio could be compensated in real time.

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Implementing DOE's as discussed already in the current section may aid in revealing the most appropriate and effective process parameters for this purpose. Such real-time course correction could provide significant advantage in terms of achieving reproducibility and yield by minimizing the number of scrap wafers and wasted runs due to unacceptable GaN crystal quality. Consequent cost reduction could be large, considering the irreproducibility and drift levels in the current GaN technology as well as the high per-wafer materials cost in GaN-based manufacturing.

3.7 Implications in terms of intrinsic chemistry

One of the advantages of the foregoing application of real-time chemical sensing and metrology for manufacturing process control is that it does not require a complete understanding of the intrinsic chemistry, and can be exploited readily. Therefore, the current debate over the relevant reaction pathway and the parasitic reactions does not seem to be a major bottleneck in GaN-based technology and manufacturing for now. However, in the long run, better understanding of fundamental mechanisms will no doubt help in terms of being able to optimize process conditions, and materials and device performance.

As discussed in Sec. 1.3, current understandings of the GaN-based MOCVD process suggest there are two independent reaction pathways, i.e., the gas phase adduct formation route and the direct surface decomposition route. Prior investigations have focused on significantly lower temperature regimes (room T. – 800 °C) than those treated here for electronic applications (>1000 °C). Modeling work performed within our research group⁶⁷ indicate that the operative process chemistry changes significantly as the

temperature is raised above 1000 °C, particularly in terms of the relative contributions of the two different reaction pathways. This can be monitored by the same methane/ethane ratio metric, since ethane can only be produced as a byproduct of the surface reaction route but not the adduct route. Further exploratory investigations are planned to elucidate these issues related to the intrinsic process chemistry, for example, as discussed in Sec. 8.1. In any case, all of our results to date indicate that the surface reaction pathway, involving direct decomposition of the metal-organic precursor on the wafer surface, leads to better crystal quality than does the adduct pathway.

TABLE 3.1. Process and tool conditions used for set A runs. Larger spacing between the showerhead and susceptor was created compared to set B and C runs by the use of 0.25 in. shorter susceptor legs.

Run#	GaN Time (min)	Pressure (Torr)	Carrier Gas (slm)	NH ₃ (slm)	TMG (sccm)	Pyrometer T. (°C)	Showerhead	Liner
G245	90	50	25	4	11	1077	F	3
G246	75	50	25	3.8	14	1082	F	9
G247	90	50	25	4.2	14	1085	F	9
G248	90	50	25	4	12	1093	F	10
G249	90	50	25	4	12	1100	F	10

TABLE 3.2. Process and tool conditions used for set B runs. The showerhead to susceptor spacing was smaller than for set A runs by the use of 0.25 in. longer susceptor legs.

Run#	GaN Time (min)	Pressure (Torr)	Carrier Gas (slm)	NH3 (slm)	TMG (sccm)	Pyrometer T. (°C)	Showerhead	Liner
G262	60	50	25	4	18	1106	F	9
G263	60	50	25	4	20	1115	F	11
G264	60	50	25	4	22	1130	F	11

TABLE 3.3. Process and tool conditions used for set C runs. The showerhead to susceptor spacing was smaller than for set A runs by the use of 0.25 in. longer susceptor legs. Also, showerheads with markedly different hole pattern were used compared to set A and B runs.

Run#	GaN Time (min)	Pressure (Torr)	Carrier Gas (slm)	NH3 (slm)	TMG (sccm)	Pyrometer T. (°C)	Showerhead	Liner
G379	90	50	15	3	15	1111	G	3
G380	90	50	15	3	15	1102	G	3
G382	95	50	15	3	20	1111	G	12
G386	90	50	15	3	20	1113	G	18

TABLE 3.4. Post-process GaN epilayer characterization for set A runs. GaN epilayer thickness was measured by PL, from which the average growth rate could be deduced. XRD rocking curve FWHM provided a measure of epilayer crystal quality. Distortion of the on-axis (002) reflection is considered to be due to screw dislocations, whereas the off-axis (102) reflection is considered to be affected by both screw and edge dislocations. Methane/ethane ratio obtained from in-situ mass spec serves as our real-time crystal quality prediction metric.

Run#	Thickness by PL (µm)	Average Growth Rate (µm/h)	Methane/Ethane Ratio	XRD FWHM at (002)	XRD FWHM at (102)
G245	0.695	0.46	1.51	269	244
G246	1.354	1.08	1.33	223	227
G247	1.553	1.04	0.71	187	169
G248	1.305	0.87	1.58	290	292
G249	0.650	0.43	1.92	330	315

TABLE 3.5. Post-process GaN epilayer characterization for set B runs. GaN epilayer thickness was measured by PL, from which the average growth rate could be deduced. XRD rocking curve FWHM provided a measure of epilayer crystal quality. Methane/ethane ratio obtained from in-situ mass spec serves as our real-time crystal quality prediction metric.

Run#	Thickness by PL (µm)	Average Growth Rate (µm/h)	Methane/Ethane Ratio	XRD FWHM at (002)	
G262	1.197	1.20	2.32	199	
G263	1.449	1.45	2.44	248	
G264	1.173	1.17	2.53	266	

TABLE 3.6. Post-process GaN epilayer characterization for set C runs. GaN epilayer thickness was measured by PL, from which the average growth rate could be deduced. XRD rocking curve FWHM provided a measure of epilayer crystal quality. Methane/ethane ratio obtained from in-situ mass spec serves as our real-time crystal quality prediction metric.

Run#	Thickness by PL (µm)	Average Growth Rate (µm/h)	Methane/Ethane Ratio	XRD FWHM at (002)	
G379	0.860	0.57	2.01	189	
G380	0.805	0.54	2.16	296	
G382	0.925	0.58	2.17	273	
G386	1.083	0.72	2.12	242	



FIG. 3.1. In-situ gas phase chemical signals from mass spec, indicative of the dynamic gas composition downstream of the reactor as a function of process steps. Shown here are the reaction byproducts methane (at amu 13) and ethane (at amu 26) through the AlN, GaN, and AlGaN layer growth steps along with the corresponding methane/ethane ratio metric derived in real time. This example is taken from run G262, the same run as in Fig. 2.3.



FIG. 3.2. Run-to-run variation in GaN epilayer crystal quality as measured by postprocess XRD shows average variation of 29 arcsec or 11 - 12% for set A runs. The distortion of the (002) peak is indicative of screw dislocations whereas that of the (102) peak is known to arise from both screw and edge dislocations.



FIG. 3.3. Real-time prediction of GaN epilayer crystal quality during growth based on insitu measurement of methane/ethane byproducts ratio by mass spec for set A runs. The metrology models show accuracies on the order of 5.1% average uncertainty for (002) peak and 4.9% for (102) peak respectively. In general, narrower XRD rocking curve peaks represent better crystal quality, so in this case, it is apparent that smaller methane/ethane ratio is preferred for better GaN crystal quality.



FIG. 3.4. Real-time prediction of GaN epilayer crystal quality during growth based on insitu measurement of methane/ethane byproducts ratio by mass spec for set B runs. The metrology model shows accuracy on the order of 2.0% average uncertainty for the (002) peak. In general, narrower XRD rocking curve peaks represent better crystal quality, so in this case, it is apparent that smaller methane/ethane ratio is preferred for better crystal quality GaN. Identical showerhead design, but a smaller showerhead to susceptor spacing (0.25 in. less), was used compared to set A runs.



FIG. 3.5. Real-time prediction of GaN epilayer crystal quality during growth based on insitu measurement of methane/ethane byproducts ratio by mass spec for set C runs. The metrology model shows accuracy on the order of 3.5% average uncertainty for the (002) peak. In general, narrower XRD rocking curve peaks represent better crystal quality, so in this case, it is apparent that smaller methane/ethane ratio is preferred for better crystal quality GaN. A completely different showerhead design, but an identical showerhead to susceptor spacing, was used compared to set B runs.



FIG. 3.6. Crystal quality prediction models for three different tool configurations in terms of the showerhead to susceptor spacing (larger vs. smaller spacing) and the showerhead design (F vs. G). It is apparent that the critical variables giving rise to a set of different metrology models are the tool configuration parameters (the showerhead-to-susceptor spacing and the specific showerhead design), not the small changes made, within each set, in temperature, gas flow rates, composition, liners, etc. Therefore, we conclude that once we define the tool configurations/geometries for our processes, we are practically defining the elements that determine the metrology/control model.

Chapter 4 Real-time precision metrology for AlGaN cap layer thickness

4.1 Sensor-based real-time metric development

It is believed that the two byproducts, methane and ethane, originate from the two parallel chemical reaction pathways to grow GaN-based material on the wafer as discussed in Sec. 1.3. One occurs in the gas phase through complex adduct species formation to form a trimer specie before finally decomposing to form GaN (or AlGaN, depending on precursors) on the hot wafer surface. This adduct pathway releases several molecules of methane as the reaction byproduct. On the other hand, the metal-organic precursor(s) can decompose directly on the hot wafer surface to grow GaN (or AlGaN). releasing primarily ethane as its reaction byproduct. Previously in Ch. 3 we showed that the methane/ethane ratio, obtained in real time during growth, can successfully predict the crystal quality of the GaN epilayer with quantitative precision (1 - 5%), which is verified by post-process XRD measurement of crystal quality. In that situation, the byproducts ratio reflected the relative amount of material produced by either path, which yields different material quality. We also note that since the two byproducts come from two parallel pathways to grow the GaN-based material on the wafer, it is expected that summing the two byproduct signals over the duration of the film growth provide a measure related to the total film thickness grown. Hence, we have applied this methodology to real-time AlGaN cap layer thickness metrology and control here.

Although we initially observed a reasonable quantitative correlation to the AlGaN thickness using the raw mass spec current signals measured at 13 and 26 amu's (as

described in Sec. 2.3.2), additional efforts were made to more accurately model the relationship between the real-time mass spec signals and the post-process XRR measurement of the actual film thickness, thus improving the precision of the real-time metrology model. In particular, by incorporating different normalization factors (α and β) described below for the raw methane and ethane signals enabled better approximation for the species' true relative partial pressures, thus ensuring that the model is insensitive to the relative contributions of methane vs. ethane paths. Additionally, normalization with respect to the 50 Torr H₂ signal measured prior to each run corrected for any sensor drifts.

Equation (4.1) describes the relationship between the partial pressure of substance "a" (PP_a) and the raw mass spec ion current for the substance at mass "b" (I_{ab}) . Basically, there are two factors relating the raw ion current observed to the true partial pressure of the substance: (1) the *material factor* (M_{ab}) which depends on the nature of the substance being detected and (2) the *analyzer factor* (A_b) which depends on the characteristics of the partial pressure analyzer.

$$PP_a = (M_{ab} \times A_b) \times I_{ab} \tag{4.1}^{72}$$

The material factor (M_{ab}), further depends on the fragmentation pattern for the particular substance and the reference gas (usually nitrogen), and the ease with which the substance can be ionized relative to the same reference gas as shown in the following equation:

$$M_{ab} = (FF_{ab} \times XF_{a})^{-1} \tag{4.2}^{72}$$

The term FF_{ab} is the *fragmentation factor* for substance "a" at mass "b". It is equal to the fraction of the total current of all ions from substance "a" which has a mass "b". The term XF_a is the *ionization probability* of substance "a" relative to nitrogen (i.e., $XF_N=1$), otherwise known as the relative *cross-section* of the substance. It is the ratio of total ion

current (for all masses) from substance "a" to the total ion current from nitrogen, both measured at the same true partial pressure. The *FF*'s for methane at amu 13 and ethane at amu 26, were estimated to be 0.04 and 0.12 respectively, based on the fragmentation patterns obtained from the NIST database.⁷³ Likewise, the *XF* values were obtained by taking the absolute cross-sections of methane (0.2975 nm) and ethane (0.5518 nm), then dividing them by that of nitrogen (0.1812 nm), which gave 1.642 for methane and 3.045 for ethane. From the *FF*'s and *XF*'s, *M*'s could be calculated using Eq. (4.2). However, the *A*'s were far more difficult to obtain. Hence, we only considered the *M*'s for methane (at amu 13) and ethane (at amu 26) here, whose values were calculated to be 15.225 and 2.737 respectively. Multiplying the methane and ethane raw mass spec signals with the respective material factors provides the following expression:

$$\alpha \left[\mathbf{S}(\mathrm{CH}_{4}) dt + \beta \right] \mathbf{S}(\mathrm{C}_{2}\mathrm{H}_{6}) dt$$
(4.3)

where α (15.225) and β (2.737) are the material factors for methane (at amu 13) and ethane (at amu 26) respectively, and $\int S(CH_4)dt$ and $\int S(C_2H_6)dt$ represent the raw mass spec current signals for methane (at amu 13) and ethane (at amu 26) integrated in real time over the AlGaN growth step as shown in Fig. 4.1. This in turn was normalized with respect to the 50 Torr H₂ current signal measured at amu 2 prior to the growth step for each run. This was an attempt to correct for the minor sensor drifts, for example, the slight run-to-run variation in signal gain and sensor sensitivity. Finally, our real-time metric for predicting the AlGaN thickness becomes:

$$\frac{1}{\mathbf{S}(\mathrm{H}_2)} \Big[\alpha \int \mathbf{S}(\mathrm{CH}_4) dt + \beta \int \mathbf{S}(\mathrm{C}_2 \mathrm{H}_6) dt \Big]$$
(4.4)

Comparison of the normalized signal to the post-process XRR measurement of AlGaN thickness generated a precision film thickness metrology model as discussed in the following sections. Furthermore, the mass-spec-based signal could now be used as our real-time film thickness metric to predict the AlGaN cap layer thickness during growth to a precision defined by the model.

4.2 AlGaN thickness variability and metrology

In terms of thickness control for the various layers within the heterostructure, controlling the AlGaN cap layer thickness is the greatest challenge. It is the thinnest layer, with a typical target thickness range of 20 - 25 nm. Figure 4.2 shows the run-to-run variation in the average AlGaN thickness measured by XRR for the HEMT heterostructure growth runs on semi-insulating SiC substrates performed without control. Unfortunately, not more than 1/3 of the runs fell within the target range of 20 - 25 nm, reflecting a large process and equipment variability. Even using the same exact tool configuration run-to-run, we observed that multiple process adjustments and wafers were needed to reach a given target.

Figure 4.3 shows the real-time sensor-based AlGaN thickness metric [see Eq. (4.4)] compared to the actual film thickness measured by post-process XRR. Linear regression model between the real-time sensor-based metric and post-process XRR measurement indicates a precision of 3.9% or 1.0 nm average uncertainty. This is a reasonable precision considering that it represents a broad thickness variation (~2X), unlikely to be encountered in a high volume manufacturing typically with fixed tool configurations and process conditions.

4.3 Precision thickness metrology for manufacturing

While the experiments above included a variety of process conditions and equipment configurations (see Table 4.1), our goal is to assess the prognosis for real-time thickness metrology and control, where equipment configurations will be fixed and nominal process settings relatively invariant. To estimate the metrology precision, we therefore filtered the data in Fig. 4.3 to specify fixed equipment and process conditions. Filtering the metrology data to restrict it to a single showerhead design (F) and a more restricted thickness range (19 - 25 nm), we are left with 7 data points as shown in Fig. 4.4. Linear regression model based on the local range data yields a precision of 1.2% or 0.26 nm. This local range metrology result demonstrates a striking level of precision for AlGaN cap layer thickness metrology: if translated into real-time end-point control, it suggests that a 20 nm cap layer could be controlled to 0.2 nm in the presence of 20 - 30% process and equipment variability.

Finally, we note that a minimal measurement error was contributed by the high resolution XRR as described in Sec. 2.4.2. Although no specific numbers could be obtained, it is expected to be significantly less than or at least on the order of the $\sim 1\%$ precision of the in-situ metrology models presented in this chapter.

4.4 Prognosis for applications

The AlGaN cap layer thickness metrology developed here demonstrates sufficient precision for use in manufacturing process control, for example in the form of run-to-run or – more straightforwardly and effectively – real-time process control. The mass spec

sensor is particularly attractive because it can be used to serve other important purposes such as FDC and process learning, which are reported in Chs. 3 and 5. The use of mass spec for manufacturing process control has already been well demonstrated in the past, for example in a 10 Torr W CVD process²⁷ discussed in Sec. 1.2.

In this work, we have demonstrated that that the same mass-spec-based thickness metrology and control can be extended into the nanoscale regime. For instance, the AlGaN cap layer (~20 nm) here is orders of magnitude thinner than the blanket W layer (>1 μ m) in the W CVD process.²⁷ This is important because the Si ULSI industry is now dealing with various kinds of ultra thin (nanoscale) layers, such as barrier layers or gate dielectrics by CVD or ALD – a challenging requirement for the precision of in-situ sensors.⁷ Not a traditional thickness monitoring sensor, mass spec metrology demonstrated here achieves nm – even atomic – precision.

Moreover, the level of methane and ethane signals here were on the order of ppm or less (relative to the largest signal, H₂ carrier gas) as seen in Fig. 2.3. In the previous work observing the HF byproduct in W CVD process (Fig. 1.4),²⁷ the reaction product was on the order of ~10% of the largest signal, the H₂ reactant. Despite the low signal levels in the present work on AlGaN MOCVD, significant precision was achieved, in part by implementing special measures such as the use of electron multiplier detection, different dwell times as a function of species detection levels, and run-to-run data normalization for any sensor sensitivity drift. As a result, both the thinner thickness and lower species detection levels have been successfully overcome without a significant loss in control capability here.

In fact, the $\sim 1\%$ metrology precision has been deemed sufficient to drive end-point process control. Although no data is currently available from a dedicated series of control experiments, a cruder form of end-point control has been routinely implemented in our AlGaN/GaN/AlN MOCVD processes. It indicates the control precision to be $\sim 1 - 2\%$ to date, which in turn increased the yield of the particular unit process step from ~31% as seen in Fig. 4.2 to near $>\sim 90\%$ with control. Meanwhile, a more complete interfacing of the sensor, MOCVD tool, and the tool controller has been realized with a LabVIEWTMbased process control program sharing the data in real time with the other components through DDETM-based communication as discussed earlier in Sec. 2.5. This enables a complete closed-loop automated process control based on precision metrology as developed here. More is to be discussed in future publications related to the control of these processes. This offers important benefits in terms of the reduced number of manual process recipe tuning runs (performed on n⁺ substrates prior to growth on semi-insulating substrates), reduced number of wasted runs/wafers, significant cost savings considering the cost of each semi-insulating SiC substrate wafers (average of ~\$3000/wafer), and the limited throughput in the current tool set.

Run#	AlGaN Time (s)	Pressure (Torr)	Carrier Gas (slm)	NH3 (slm)	TMG (sccm)	TMA (sccm)	Pyrometer T. (°C)	Showerhead	Liner
G288	259	50	25	4	5	12	1107	F	10
G289	259	50	25	4	6	12	1108	F	10
G290	260	50	25	4	7	12	1115	F	10
G379	180	50	15	3	15	24	1111	G	3
G380	138	50	15	3	15	24	1102	G	3
G383	77	50	15	3	20	44	1106	G	12
G386	80	50	15	3	20	47	1113	G	18
G387	59	50	15	3	20	47	1107	G	18
G406	65	50	15	3	16	46	1147	F	9
G409	64	50	15	3	15	38.3	1140	F	14
G413	58	50	15	3	19	55	1138	F	17
G416	54	50	15	3	20	48	1126	F	12

TABLE 4.1. Process and tool conditions used for the AlGaN part of theAlGaN/GaN/AlN HEMT heterostructure growth runs.



FIG. 4.1. In-situ methane and ethane signals from mass spec during an AlGaN cap layer growth period. The current growth step (i.e., GaN or AlGaN) was determined from the relevant equipment-state changes (e.g., TMA line open/close signal). Areas under each curve were integrated over the duration of the AlGaN growth period to generate the real-time film thickness metric. Note that in this case the ethane signal did not produce a noticeable change in magnitude going from GaN to AlGaN layer growth, which seem to indicate that the ethane byproduct, thus the surface reaction path, may be relatively insensitive to the TMA-based chemistry. However, further study is required for clearer understanding of the chemistry.



FIG. 4.2. Run-to-run variation in product AlGaN cap layer thickness as determined by XRR. Shown are the data from all HEMT heterostructure growth runs performed on semi-insulating SiC substrates during an arbitrary period in the year 2003. Considering that typical thickness process windows are in the range of 20 - 25 nm, these runs could imply a yield as low as ~31%.



FIG. 4.3. AlGaN cap layer thickness metrology over a broad thickness range (Δ ~17 nm). The real-time film thickness metric based on methane and ethane signals measured by mass spec exhibited a strong linear correlation (3.9% precision) to the actual film thickness grown, as measured by post-process XRR.



FIG. 4.4. AlGaN cap layer thickness metrology within the thickness range of ~ 6 nm. The real-time film thickness metric based on methane and ethane signals measured by mass spec exhibited a strong linear correlation (1.2% precision) to the actual film thickness grown, as measured by post-process XRR.

Chapter 5 Real-time prediction of GaN photoluminescence quality and pre-growth contamination control

5.1 Sensor-based real-time metrics development

Details of the mass spec sensing and metrology development are the same as described in the previous Secs. 2.3, 3.2, and 4.1. In summary, In-situ mass spec sensing of the 50 Torr MOCVD growth process provided dynamic, real-time gas phase chemical signals as a function of the process cycle. Characteristic ion current signals were obtained for H₂ (carrier gas), NH₃ (column V precursor), N₂ (fragmentation product from NH₃), H₂O (background impurity), CH₄ (reaction byproduct), C₂H₆ (reaction byproduct), C (background impurity), O₂ (background impurity), and other yet unknown impurity species (e.g., at amu 55). In particular, it is demonstrated in this chapter that the background impurity levels measured at amu's 18 (H₂O), 32 (O₂), and 55 (unknown impurity) correlate to the PL band-edge and deep-level intensities with reasonable precision (~5 – 20%). Note that the actual metrics for run-to-run comparison were obtained by taking the raw mass spec current signals at amu's 18, 32, and 55, then normalizing them with respect to the 50 Torr H₂ current signal measured at amu 2 prior to the growth step for each run as the following:

$$\frac{S(H_2O)}{S(H_2)}, \frac{S(O_2)}{S(H_2)}, \frac{S(amu55)}{S(H_2)}$$
(5.1)

This was an attempt to correct for the minor sensor drifts, for example, the slight run-torun variation in signal gain and sensor sensitivity as similarly done for the AlGaN cap layer thickness metric in Eq. (4.4).

5.2 Real-time prediction of GaN photoluminescence qualities and metrology

5.2.1 Prediction during GaN epilayer growth

In Ch. 3, it was demonstrated that the real-time methane/ethane ratio enabled prediction of GaN epilayer crystal quality during growth to a precision 2 - 5%, which was verified by the post-process measurement of crystal quality by XRD. Here we demonstrate that the same methane/ethane ratio metric, obtained during GaN epitaxy, can also predict PL band-edge intensity to within ~5% precision. This is shown in Fig. 5.1 for the same set of four runs, for which the crystal quality correlation was demonstrated in Fig. 3.5. Moreover, the correlation is such that by going to lower methane/ethane ratio we improve material quality as seen in both XRD and PL. This has further implications in terms of the intrinsic chemistry, which are discussed in the following Sec. 5.3.

In-situ mass spec sensing also allowed monitoring of the background impurity species during GaN epitaxy as discussed already in the previous section. In particular, we focused our attention on the gas phase residual H₂O and O₂ because they are the common impurities in other semiconductor processes, and in part because oxygen (O from either H₂O or O₂) is known to act as an unintentional shallow donor in GaN along with other types of defects such as nitrogen vacancies.⁷⁴ Correlations showed that the PL band-edge intensity suffered (i.e., lower) with more residual H₂O present during GaN epitaxy (Fig. 5.2) and the PL deep-level intensity suffered (i.e., higher) with more residual O₂ present during a low gas phase impurity condition within the reactor is critical for high quality GaN material growth. We

also realized that such conditions must be established prior to the GaN growth step itself because there is little room for course correction as far as removing the impurities in a timely fashion is concerned.

For completeness of the discussion, we note that there are total of four combinations available from the residual H₂O and O₂ levels measured by in-situ mass spec, and bandedge and deep-level intensities measured by post-process PL, only two of which are addressed above. The other two combinations (i.e., band-edge vs. O₂ level, deep-level vs. H₂O level) did not produce appreciable correlations. Little physical explanation is currently offered for the particular choice of two working combinations (i.e., band-edge vs. H₂O level, deep-level vs. O₂ level) in part due to the complexity of how both the band-edge and deep-level in GaN are affected by numerous factors (i.e., substrate and nucleation layer qualities, processing, impurities). However, the goal here is to devise a pragmatic solution based on correlations that work, in an effort to improve the material quality, in this case as measured by PL.

5.2.2 Prediction during pre-growth steps

Hence, our attention was directed to the pre-growth steps, where we still have a chance to effectively reduce the impurity levels within the reactor prior to the actual film growth. In particular, we focused on the pre-growth reactor purge steps (room temperature purge, heating, followed by high temperature purge), where we attempt to bake away the impurities with high temperature (~1100 °C) and purging gas (H₂). Details of these pre-growth steps are described in Sec. 2.1. Progress of the reactor purge is monitored in real time using the mass spec, and the impurity levels were noted at the end

of the high temperature purge step, which occurred immediately prior to the actual HEMT heterostructure growth, for correlation to post-process PL quality measurements. Not surprisingly, the residual H₂O level measured at that point was found to correlate to the PL band-edge intensity measured post-process as shown in Fig. 5.4. Better quality material (as seen in higher band-edge intensity) was obtained when the pre-growth residual H₂O level was lower, with the correlation accurate to \sim 7%. Note that these include the same set of runs as shown in Fig. 5.1.

PL band-edge intensity was also found to correlate to another impurity measured at amu 55 (unknown specie) as shown in Fig. 5.5. However, in this case, better quality material (as seen in higher band-edge intensity) was obtained with *higher* (not lower) impurity level detected prior to growth. Further study is required to determine the exact identity of the unknown species at amu 55. It is conjectured that this species is some type of residual impurity compound formed by a combination of C, H, and O, because its steadily decreasing behavior through the entire process cycle parallels that for C and O.

High band-edge intensity alone does not mean anything unless accompanied by low deep-level (yellow) luminescence. Therefore, the two must be optimized concurrently: typically resulting in a band-edge to deep-level ratio of >1000. We found that by normalizing the pre-growth residual O_2 level to the epilayer growth rate (both of which can be obtained in real time from mass spec), PL deep-level can be predicted as shown in Fig. 5.6. Better quality material (as seen in lower deep-level intensity) was obtained when the pre-growth residual O_2 level was lower and the growth rate was lower, with the correlation accurate to ~19%. Although the correlation here is less precise compared to the case of PL band-edge intensity, this offers an important means to predict and possibly

control GaN deep-level concurrent with the band-edge intensity, because the two parameters put together are critical as a measure of GaN material quality.

Finally, we note that a minimal measurement error was contributed by the high resolution PL as described in Sec. 2.4.3. Although no specific numbers could be obtained, it is expected to be significantly less than the 5 - 20% precision of the in-situ metrology models presented in this chapter.

5.3 Implications in terms of intrinsic chemistry

One of the key results demonstrated here (Fig. 5.1) was that the same methane/ethane ratio metric from mass spec used to predict GaN epilayer crystal quality (measured by XRD) could also be used to predict PL band-edge intensity with similar quantitative precision (~5%). Moreover, the correlation is such that by going to lower methane/ethane ratio we improve material quality as seen in both XRD and PL. In terms of chemistry, this would mean that, of the two chemical reaction pathways to grow GaN-based material on the wafer, the surface reaction pathway with direct decomposition of the precursors (involving ethane byproduct) is preferred over the gas phase reaction pathway with complex adduct formation (involving methane byproduct). This was discussed in detail in our earlier work on real-time crystal quality prediction in Ch. 3, and it is reaffirmed here with the addition of PL results. Therefore, the results to date indicate that the surface reaction pathway, identified by its ethane byproduct, is the preferred route to grow high quality GaN-based material as verified by the two highly important post-process material characterization techniques – i.e., XRD and PL.

5.4 Pre-growth contamination control

We also demonstrated here a contamination control methodology that assures a low gas phase impurity condition prior to material growth (Figs. 5.4 - 5.6). Implementing pre-growth reactor purge with high temperature and purging gas, and monitoring the reduction in the relevant gas phase impurity levels allowed us to guarantee acceptable product quality as seen in post-process PL. This is important because it provides an opportunity to implement the solution in a timely fashion (i.e., pre-growth as opposed to during growth) thus significantly increasing its effectiveness in terms of achieving acceptable material quality. In terms of the metrology precision presented here, it varied anywhere from ~5% to ~19% depending on the model. However, the goal here is not a precision course correction as done for other figures of merit such as the AlGaN cap layer thickness control, but a rather general fault detection that leads to routine contamination control to guarantee some required conditions *before* growth by preparing an acceptably low impurity growth environment. This is accompanied by detection of occasional process and equipment excursions as shown in the following Ch. 6, for which the goal is the same.



FIG. 5.1. Real-time prediction of GaN PL band-edge intensity during growth based on in-situ mass spec measurement of methane/ethane byproducts ratio (precision 4.8%). The four runs shown here correspond to the same four runs presented in Ch. 3 on crystal quality prediction, where it was shown that the same methane/ethane ratio metric predicts GaN epilayer crystal quality to 3.5% verified by post-process XRD. Moreover, the correlation is such that by going to lower methane/ethane ratio we improve material quality as seen in both XRD and PL.



FIG. 5.2. Correlation of the gas phase residual H₂O level within the reactor during GaN epitaxy to the GaN PL band-edge intensity measured post-process. Better quality material (as seen in higher band-edge intensity) was obtained when the residual H₂O level was lower.



FIG. 5.3. Correlation of the gas phase residual O_2 level within the reactor during GaN epitaxy to the GaN PL deep-level intensity measured post-process. Better quality material (as seen in lower deep-level intensity) was obtained when the residual O_2 level was lower.



FIG. 5.4. Correlation of the gas phase residual H_2O level within the pre-growth reactor to the GaN PL band-edge intensity measured post-process. Better quality material (as seen in higher band-edge intensity) was obtained when the pre-growth residual H_2O level was lower with the correlation accurate to 6.6% here.



FIG. 5.5. Correlation of the gas phase residual impurity level, measured at amu 55, within the pre-growth reactor to the GaN PL band-edge intensity measured post-process. Better quality material (as seen in higher band-edge intensity) was obtained with *higher* (not lower) impurity level detected prior to growth with the correlation accurate to 10% here. Further study is required to determine the exact identity of the unknown specie at amu 55 and its effect on the process.



FIG. 5.6. Correlation of the gas phase residual O_2 level within the pre-growth reactor to the GaN PL deep-level intensity measured post-process. Better quality material (as seen in lower deep-level intensity) was obtained when the pre-growth residual O_2 level was lower with the correlation accurate to 19% here. Although the correlation here is less precise compared to the case of PL band-edge intensity, this offers an important means to predict and possibly control GaN deep-level concurrent with the band-edge intensity, because the two parameters put together are critical as a measure of GaN material quality.

Chapter 6 Additional real-time fault detection and management applications

6.1 Pre-growth reactor purge step fault detection and management

The same mass spec sensor that provides all of these useful metrology models for process control and pre-growth contamination control, as described in the previous chapters, can also be used to drive fault detection. In fact, mass spec has been by far the most pervasive chemical sensor for successful fault detection in APC in the Si ULSI industry.¹ Here, we developed a number of such fault detection applications based on clear chemical signatures for process and equipment faults which potentially lead to unacceptable product quality. For instance, we monitored the progress of the reactor purge during the pre-growth steps as described in the previous chapter and shown in Fig. 6.1. Part (a) of the figure shows H₂O vapor desorbing from the unconditioned walls of a brand new liner as soon as the temperature ramp begins. In addition, we observed impurity desorption from a dirty susceptor in the form of N₂ during the high temperature purge, also shown in part (a). However, such impurity evolutions were not observed with a well conditioned liner and a clean susceptor as shown in part (b). These kinds of real-time indications as in part (a) clearly correlated to unacceptable material quality by PL, and they indicated a need for measures to correct the root cause.

While adequate conditioning of a brand new liner could be achieved simply by extending the duration of the pre-growth purge steps, faults based on cracking of, or impurity coatings on, the susceptor required more extensive solutions to correct them since those kinds of impurities (C from the exposed graphite or other undesirable impurities desorbing from the susceptor) tend to be from a semi-infinite source which degrades film quality. Thus, we implemented replacement of the susceptor followed by a dedicated bake-out conditioning run prior to the next actual HEMT heterostructure growth run. The solution measures described here resulted in a well conditioned liner and a clean susceptor, from which no signatures of faults were observable as shown in Fig. 6.1(b), and they usually resulted in improvement in product material quality in the subsequent runs.

6.2 In-growth mass flow controller fault detection and management

There have also been cases where the upstream mass flow controllers (MFC's) for delivering various gases into the reactor failed in the middle of the growth process as shown in Fig. 6.2. In this case, failure of the NH₃ MFC during GaN epilayer growth was detected by the mass spec, while the main tool controller indicated a normal status. The real-time signatures indicating large disturbances (up to ~3 orders of magnitude) in the NH₃ concentration within the reactor were immediately noticed by the process engineer, and were followed by a series of manual tests as indicated by segments A, B, and C for trouble-shooting. Segment A indicates a test where the isolation valve between the mass spec and the reactor was closed for a period of ~2 min. Stable NH₃ signal (still remaining high due to the trapped volume within the sampling inlet of the sensor) during this period as well as the time scale for each sensing scan (10.353 s) confirmed that the disturbances were real physical effects and not electrical noise. Segments B and C indicate a series of MFC flow variation tests where the set point for the MFC flow rate was altered between a high value (80% for B) and a low value (40% for C). Results of the test indicate that the
MFC failed to perform properly for low flow set point conditions. Needless to say, postprocess characterization results of the product material from this run were far from acceptable. The MFC in question was replaced immediately and both the sensor signals as well as the future product materials themselves indicated that the fault was successfully resolved.

6.3 In-growth precursor source depletion fault detection and management

Finally, Fig. 6.3 shows sensing during a run where the reaction byproduct (CH₄ and C_2H_6) levels were significantly lower than the usual. Again, this was immediately noticed by the process engineer monitoring the sensor output in real time. Although the unusually low byproduct levels do not necessarily correspond directly to precursor source depletion, it certainly provides a useful real-time signature that leads to more in-depth fault classification in a timely manner. In this case, insufficient growth of product film seen post-process matched the real-time fault detection by the sensor, and led to examination of a limited number of possible sources for the fault, which included precursor source depletion and excessive deposition within the showerhead. Once the root cause for the fault was identified - in this case precursor source depletion – an appropriate solution was implemented to correct the problem (i.e., immediate replacement of the precursor source bottle).

Normally, if the reactants are originally in the form of gas phase, the gas bottle pressures provide a means to closely follow their usage levels over time. However, in this case and in increasing number of semiconductor processes today, that is not the case. The metal-organic precursors (TMA and TMG), originally in the liquid phase and kept in

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temperature controlled bubblers, are delivered to the reactor via the saturated carrier gas (H₂). Accurate monitoring of the run-to-run usage level becomes more difficult. We may be able to deduce it by monitoring the reactant and/or the reaction byproduct levels upstream or downstream of the wafer. One of the options may be the use of acoustic sensors, installed between the bubbler and the reactor, to monitor the precursor concentration in the *upstream* delivery line. This would also allow real-time closed-loop control to maintain desired level of concentration in the face of run-to-run drift in concentration due to changes in the liquid source vapor pressure with over-time usage.⁷⁷ Here, the mass spec sensor monitoring the growth reaction far *downstream* of the wafer provided an additional capability to detect such faults in real time. Thus, although the former option may be a more elegant solution, the latter option is extremely attractive because it allows for multiple applications with both process- and wafer-state control, and other types of real-time fault detection applications at the same time with a single sensor. Nevertheless, these kinds of in-situ sensors have proven to be extremely valuable to drive fault detection as demonstrated here.



FIG. 6.1. An example of real-time fault detection based on clear chemical signatures for process and equipment faults which potentially lead to unacceptable product quality. (a) Desorption of H_2O vapor from the unconditioned walls of a brand new liner as soon as the temperature ramp begins, followed by desorption of impurity coating from a dirty susceptor in the form of N_2 during the high temperature purge. (b) Such impurity evolutions were not observed with a well conditioned liner and a clean susceptor. These kinds of real-time indications as in (a) clearly correlated to unacceptable material quality by PL, and they indicated a need for measures to correct the root cause, such as through extended pre-growth contamination control and replacement of corresponding tool parts (e.g., susceptor).



GaN Growth

FIG. 6.2. An example of real-time detection of an equipment excursion in the middle of process that led to unacceptable material quality. Failure of an NH₃ MFC was immediately detected by the mass spec during GaN epilayer growth from the real-time signatures indicating large disturbances in the NH₃ concentration within the reactor. Segment A indicates a manual test where the isolation valve between the mass spec and the reactor was closed for a period of ~2 min. Stable NH₃ signal (still remaining high due to the trapped volume within the sampling inlet of the sensor) during this period as well as the time scale for each sensing scan (10.353 s) confirmed that the disturbances were real physical effects and not an electrical noise. Segments B and C indicate a series of MFC flow variation tests where the set point for the MFC flow rate was altered between a high value (80% for B) and a low value (40% for C). Results of the test indicate that the MFC failed to perform properly for low flow rate set point conditions. The MFC in question was replaced immediately and both the sensor signals as well as the future product materials themselves indicate that the fault was successfully resolved.



FIG. 6.3. Mass spec sensing during a run where the reaction byproduct (CH₄ and C₂H₆) levels were significantly lower than the usual. This was correlated to the little growth of product film seen post-process, which led to examination of a limited number of possible sources for the fault. Once the root cause was identified to be the untimely precursor source depletion, the precursor source bottle was immediately replaced. The segment labeled "EM off" indicates a test where the mass spec electron multiplier was turned off for ~2 min and then turned back on to confirm that it was functioning properly.

Chapter 7 Conclusions

7.1 W CVD metrology and control

In-situ mass spec sensing was implemented downstream in a 10 Torr H_2/WF_6 W CVD process to develop a real-time thickness metrology. HF byproduct generation and H_2/WF_6 reactants depletion were observed in real-time mass spec signals and used to derive predictors of film thickness in synchronism with relevant equipment-state signals. Nearly 40 single-wafer runs have been performed to investigate the precision of the mass-spec-based thickness metrology under different sets of conditions: (1) a fixed process condition, (2) intentionally introduced run-to-run process temperature drift, and (3) run-to-run deposition time variation. Based on real-time integration of the HF byproduct signal from the sensor and its comparison to post-process ex-situ measurement of the film weight and thickness, it was demonstrated that the precision of this real-time film thickness metrology delivers better than 1% average uncertainty in all cases.

This represents a significant improvement over our previous metrology results in sub-Torr W CVD processes (i.e., 7% average uncertainty in H_2/WF_6 process and 2% average uncertainty in SiH₄/WF₆ process). The improved accuracy is attributed to the increased reactant conversion rate of around 30%, compared to 3% in H_2/WF_6 process and 20% in SiH₄/WF₆ process. The metrological precision – better than 1% average uncertainty – is consistent with industry and roadmap requirements for manufacturing application of APC, particularly in the form of real-time end-point control. Furthermore, we anticipate that the high throughput of manufacturing tools will improve chamber wall conditioning reproducibility compared to our experiments, leading to further improvement of the metrological precision.

The availability of an information-rich, in-situ chemical sensor – mass spec – capable of real-time, high precision process- and wafer-state metrology, expands sensor applications for course correction to include real-time as well as run-to-run control, with benefits in compensation for short-term variability as well as long-term systematic drift in process and equipment. Because mass spec is already a widely deployed sensor for FDC, it promises dual-use in both components of APC: course correction and fault management.

7.2 AlGaN/GaN MOCVD metrology and control

The same methodology proven in the prototypical case of W CVD metrology and control was applied in an industry development project for GaN-based semiconductor HEMT growth at Northrop Grumman Electronic Systems, in hopes of achieving process reproducibility sufficient for manufacturing. In-situ mass spec sensing was implemented in 50 Torr AlGaN/GaN/AlN HEMT heterostructure growth processes on 2 in. semiinsulating SiC substrate wafers. Dynamic chemical sensing through the entire process cycle, carried out downstream from the wafer, revealed generation of methane and ethane reaction byproducts in real time, in addition to other residual gas species present as impurities within the reactor. In particular, our process chemistry model suggested that the methane and ethane byproducts reflect the two *parallel* reaction pathways leading to GaN-based materials growth, namely the gas phase adduct formation route and the direct surface decomposition of the metal-organic precursor, respectively. Assuming that both pathways contribute in the MOCVD process and the uncertainty regarding which pathway would result in the growth of better quality material, real-time wafer-state metrics were derived based on the chemical signals for real-time prediction and control of both the critical thin film thicknesses and important intrinsic material qualities.

Real-time prediction and control of GaN epilayer crystal quality

Using the methane/ethane ratio, GaN epilayer crystal quality was shown to be predictable in real time during growth with quantitative precision of 2 - 5%. This was verified by post-process XRD using the FWHM of GaN on-axis (002) and off-axis (102) rocking curve peaks as measures of crystal quality. The same correlation was shown using three different tool configurations with combination of different showerhead designs and varied spacing between showerhead and susceptor.

The correlation shown here between real-time wafer-state metric based on the sensor and post-process product quality represents a significant advantage for GaN technology development in that it can be utilized in DOE's to quickly identify optimal range of process conditions for best product quality. This offers a systematic methodology to improve/tune GaN-based manufacturing processes with drastically reduced turn-around time and cost. The results also promise benefit to manufacturing process control in the growth of GaN-based heterostructures, both in terms of fault detection and potentially course correction as well, opening the door to the efficiencies and cost benefits of APC.

These results have further implications in terms of the intrinsic chemistry in that the two byproducts, methane and ethane, are known to be associated with the two different reaction pathways leading to GaN growth (i.e., gas phase adduct formation route and direct decomposition of precursor on surface, respectively). The fact that smaller

methane/ethane ratio during process consistently yields better crystal quality GaN film suggests that the surface reaction pathway involving direct decomposition of the metalorganic precursor produces higher quality GaN material than does the adduct pathway.

Real-time precision metrology for AlGaN cap layer thickness

Assuming that both pathways contribute in the MOCVD process, we monitored and integrated the methane and ethane signals in real time to derive a real-time film thickness metric. Integrating the sum of the two byproducts signals in this manner through the AlGaN growth period (~1 min or less) enabled us to predict the AlGaN cap layer thickness (~20 nm) to within ~1% or ~0.2 nm precision. This was verified by post-process XRR measurements averaged over the 2 in. wafer.

Similar use of mass spec for manufacturing process control has already been well demonstrated in the past, for example, in the W CVD processes discussed earlier in the same dissertation. However, the AlGaN cap layer thickness metrology developed here represents a significant improvement in capability of such in-situ sensor-based processand wafer-state metrology, namely thickness precision at atomic scale (and 1% of total thickness) using byproduct signals at the ppm levels. Furthermore, ~1% metrology precision has been deemed sufficient to drive real-time end-point process control, and it is currently implemented and used routinely in our AlGaN/GaN/AlN MOCVD processes. This offers important benefits in terms of the reduced number of manual process recipe tuning runs, reduced number of wasted runs/wafers, significant cost savings (especially considering the \$3000 average cost for each 2 in. semi-insulating SiC substrate wafer), and the limited throughput available in our development tool.

Real-time prediction of GaN photoluminescence quality, pre-growth contamination control, and additional real-time fault detection and management

In addition, using the methane/ethane ratio, material quality as measured by postprocess PL band-edge intensity was shown to be predictable in real time during growth with quantitative precision of \sim 5%. This goes hand in hand with the previously demonstrated GaN epilayer crystal quality prediction (to \sim 5% precision verified by postprocess XRD) using the same methane/ethane byproducts ratio. Both correlations indicate that better quality material is obtained for lower methane/ethane ratio. Again, they suggest that, of the two chemical reaction pathways to grow GaN, the surface reaction pathway with direct decomposition of the precursors (identified by the ethane byproduct) is preferred over the gas phase reaction pathway with adduct formation (identified by the methane byproduct).

Correlations seen between pre-growth gas phase impurity levels within the reactor and post-process PL qualities suggested that low gas phase impurity condition is critical for high quality GaN material growth. Specifically, better quality material (as seen in higher band-edge intensity) was obtained when the pre-growth residual H_2O level was lower, and better quality material (as seen in lower deep-level intensity) was obtained when the pre-growth residual O_2 level was lower. Based on these results a contamination control methodology was developed that assures a low gas phase impurity condition prior to material growth. Implementing pre-growth reactor purge with high temperature and purging gas, and monitoring the reduction in the relevant gas phase impurity levels allowed us to guarantee acceptable product quality as seen in post-process PL. These real-time fault detection and contamination control activities have been accompanied by detection of the more infrequent process and equipment excursions, for which the goal is the same.

In summary, the real-time fault detection and contamination control based on impurity levels monitoring, combined with the real-time course correction activities based on methane/ethane byproducts ratio and the time-integrated film thickness metric, have made significant contributions to our materials and process development efforts in terms of improved material quality and yield. These types of APC activities are now in routine use for the GaN-based semiconductor processes at Northrop Grumman Electronics Systems, with the prognosis for applications in other types of processes as well. Results have been presented at various international symposia^{75,76,78-80} with significant audience interest from both academia and the industry, and they are expected to be submitted for journal publications in the near future.⁸¹⁻⁸³

Chapter 8 Future Work

8.1 Spatially-resolved local sensing

All of the results in the dissertation were obtained from mass spec sensing at a location *downstream* of the deposition reaction occurring on the wafer. Sensing at this location has several important advantages, one of which is that, from a manufacturing point of view, it offers an optimal location without interfering with the process and equipment itself. The sensor and its sampling system need not be removed after each run, and they only require minimal periodic maintenance if proper procedures are followed for each process sensing. Nevertheless, while the downstream location offers the stability and robustness for day-to-day manufacturing, we believe a more sophisticated sensing scheme is required for other purposes, such as to understand the GaN intrinsic process chemistry.

With that in mind, I have designed – and currently have acquired all of the parts, ready to be assembled for experiments – a *spatially-resolved local sampling system* as shown schematically in Fig. 8.1. It is designed to utilize a 0.05-mm-i.d. x 0.1-mm-o.d. x \sim 21-in.-long quartz capillary to sample gases from the region between the showerhead and the susceptor. Materials (e.g., quartz capillary, silicone o-rings) for the different parts of the apparatus were chosen to withstand the reasonably high temperature within the reactor, and conductances of the individual quartz and stainless steel tubing parts were carefully designed to produce optimal pressure within the mass spec closed ion source with reasonable response time. As indicated on the figure, the xz-direction motion device in front of the mass spec, together with the z-direction linear motion device for the

capillary pivot point control, allows us to sample from specific locations between the showerhead and the susceptor. Moreover, since the linear motion devices are independently controlled by manual actions, the sampling location can be varied in real time during process.

The purpose of this spatially-resolved local sensing is to better understand the intrinsic process chemistry and use it to design our processes and equipment configurations to optimize product material quality. In particular, we discussed modeling of the process chemistry earlier in Sec. 1.3, where we recognized the two possible reaction pathways to grow GaN-based materials: one occurring in the gas phase through a complex adduct formation and the other occurring on the surface through direct decomposition of the metal-organic precursor. Furthermore, according to the modeling work performed within our research group,⁸⁴ it is suggested that their relative contribution varies as a strong function of temperature. This raises intriguing questions because it is known that there exists a steep temperature gradient across the showerhead. Thus, in principle, such a variation of temperature across the showerhead will affect the overall process chemistry in terms of the relative contributions of the two reaction pathways. This in turn can potentially impact the resulting material quality across the wafer because it is already demonstrated in Chs. 3 and 5 that the surface reaction pathway (identified by its ethane byproduct) produces better quality material than the gas phase counterpart (identified by its methane byproduct).

Preliminary studies have already indicated excellent prognosis for the use of local sensing for such purposes. Simulation (by Parikh and Adomaitis)⁸⁴ of our typical GaN growth process revealed a significant variation across the showerhead in temperature and

the mole fractions of dimethylgallium adduct (DMGA), [(CH₃)₂Ga:NH₂], from the gas phase reaction route and TMG from the surface route. Ratio of the two intermediate species mole fractions (i.e., DMGA/TMG indicative of the relative contributions of the two reaction paths similarly to the methane/ethane ratio discussed in Chs. 3 and 5) predicted material quality (as measured by PL) variation across the wafer, which matched the results from an actual growth run performed under identical process conditions. Readers are referred to the relevant future publications by Parikh and Adomaitis for details of the modeling and simulation. However, these kinds of spatial variation of process- and wafer-state characteristics seen in the horizontal direction (x-direction as defined in Fig. 8.1) and their interdependences offer an intriguing application for the spatially-resolved local sensing with potentially significant understanding and benefits in terms of process and equipment design optimization.

It is also of high interest to be able to sense species as a function of the vertical spacing between the showerhead and the susceptor. For instance, the actual species near the hot wafer surface – thus effectively determining the growth – may be different from the species immediately exiting the showerhead. This is of interest because our modeling⁸⁴ suggests that at higher temperatures the surface reaction pathway is expected to be more dominant than the gas phase pathway, and that the spontaneously formed TMG adduct, (CH₃)₃Ga:NH₃, can reverse back to its original constituents (NH₃ and TMG) to ultimately favor the surface reaction path (see Fig. 1.12). We hope that these kinds of spatially-resolved local sensing will result in better understanding of the intrinsic process chemistry and guide us in designing our process and equipment for optimal product material quality and uniformity across the wafer.

8.2 Design of experiments for GaN crystal quality optimization

A number of real-time wafer-state metrics were developed in this dissertation work including the methane/ethane ratio to predict/control GaN epilayer crystal quality, timeintegrated methane and ethane signals for precision control of AlGaN cap layer thickness, etc. Since they are based on real-time in-situ metrology, they can be exploited for realtime control of the MOCVD growth process in the context of APC as discussed already in the dissertation. Furthermore, attributed to the same reason, they can also be exploited for a significantly reduced set of DOE's since the metrics allow for real-time feedback of wafer-state information, which would otherwise be only available post-process. This would be especially useful in the case of material quality prediction. For instance, it was discussed in Sec. 3.6 how the real-time methane/ethane ratio metric can be used for a single DOE to find optimal process conditions for better crystal quality, as well as PL band-edge intensity as discussed later in Sec. 5.2.1. Readers are referred back to the same sections for details of the idea for the future works. Nevertheless, we find enormous value in using these real-time metrics as a systematic methodology to improve/tune GaN-based processes, and DOE's are continuously being implemented.



FIG. 8.1. Schematic representation of an experimental setup for spatially-resolved local sensing by the same mass spec system used to achieve metrology and control at the downstream location (see Fig. 2.1). A long quartz capillary, together with two motion devices, allows sensing at specific locations between the showerhead and the susceptor, contributing to better understanding of the intrinsic process chemistry occurring near the actual growth region.

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