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Extreme Ultraviolet Radiation Pulsed Atom Probe Tomography of III-Nitride Semiconductor Materials

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to the experimental parameters, the EUV radiation-triggered APT (EUV APT) produces no significant variation in the measured composition over the range of experimentally attainable gallium charge-state ratios. Additionally, the Mg doping concentration values from EUV APT agreed with those obtained by other characterization techniques. The low EUV photon fluence used in these measurements does not appear capable of generating ions via the commonly accepted bulk thermal model, suggesting a different evaporation mechanism.

INTRODUCTION

Laser-pulsed atom probe tomography (LAPT) has received considerable attention in recent years as an analytical method to produce three-dimensional (3D), sub-nanometer-resolved chemical maps of metals, semiconductors, glasses, superconductors, oxides, and even biological materials.¹⁻³ In LAPT, a sample material is shaped into a sharp specimen "tip" with an apex radius typically ranging from 10 to 50 nm. The tip is then held at cryogenic temperatures (20-100 K) and electrically biased with a direct current (DC) standing voltage under ultrahigh-vacuum conditions. The DC standing voltage is carefully chosen to be just below the threshold for field ion evaporation.²⁻⁸ Due to the high DC standing voltage and the small radius at the tip's apex, the electric field strength at the vacuum/tip interface is on the order of tens of V/nm. In a state-of-the-art conventional laser atom probe, a pulsed, focused laser (typical wavelength 355 or 532 nm) is used to induce thermal transients that trigger controlled field ion evaporation from the tip. Each field-evaporated ion is accelerated toward the detector, where its time of flight (TOF) and impact position are recorded. The identities of the ions are inferred from the TOF data and their origination location are extracted with back-projection algorithms. The accumulated dataset of TOF and detector hit position is then used to numerically generate a 3D "reconstruction" of the specimen.^{2–8} In general, the LAPT process is based on transient, laser-induced heating^{9–12} and its efficiency will depend on such specimen-specific properties as optical absorption, heat capacity, and both thermal and electrical conductivities in the presence of a high, static electric field.

Excitation wavelengths in LAPT instrumentation have progressed from the near-infrared and visible to the ultraviolet region of the spectrum. This progression to ultraviolet wavelengths produced improved results, e.g., better mass resolution and signal-to-noise ratio in APT mass spectra.^{13,14} Recently, we described in detail a new atom probe tomography (APT) method, where instead of using visible or nearultraviolet (NUV) laser pulses, we used extreme ultraviolet (EUV) light pulses to successfully trigger controlled field ion

Received:September 25, 2020Revised:January 6, 2021Published:January 20, 2021





emission from amorphous SiO₂ specimens.^{15,16} The EUV photon energy used in those experiments was ~42 eV (λ = 29.6 nm), which is above the work function, ionization potential, and band gap of any material. In those measurements, an EUV fluence (pulse energy per unit area) of $\sim 5 \times$ 10^{-4} J/m² was enough to cause measurable field ion emission. Importantly, such photon fluence roughly corresponds to one EUV photon incident on the high-curvature region of the tip per pulse and appears unlikely to generate ions via the commonly accepted bulk thermal model.¹⁷ Instead, a different evaporation mechanism might be taking place, but the exact mechanism is not yet understood. The previous reports focused on a model dielectric material, SiO2, which is amorphous and an excellent electrical insulator. Here, we are interested in understanding whether, under similar conditions, EUV radiation-triggered APT (EUV APT) is capable of interrogating III-nitride semiconductor materials, which are of technological relevance in the field of optoelectronics. This is particularly important because LAPT using conventional visible or NUV light sources is known to present significant compositional biases depending on the experimental parameters used in each experiment.¹⁸

The fact that EUV APT was able to trigger ion emission from insulating samples, such as SiO₂, does not imply that it will be able to do so from a completely different class of materials such as III-nitride semiconductor samples. The electrical, thermal, optical, and structural properties of these materials are significantly different. As an example, the previously studied SiO₂ samples were amorphous, while the GaN samples are crystalline. With regards to optical properties, GaN is absorptive and SiO₂ is transparent for NUV light, while both materials are absorptive for EUV wavelengths. Additionally, the electrical resistivity of SiO2 is several orders of magnitude higher than that for GaN, and the thermal conductivity for GaN is about two orders of magnitude higher than the one for SiO₂.²⁸⁻³⁰ All of these differences in the materials properties, in addition to the low EUV photon flux, question whether EUV APT will indeed be able to trigger field ion emission from semiconductor samples.

The interest in III-nitride materials is based on the fact that these materials enable key applications in the field of optoelectronics since they can be used as single photon sources, laser diodes, and light-emitting diodes, among others.³¹⁻³⁴ Because the performance of these devices is dependent on the defect densities and element clustering, LAPT was originally used as a nanoscale characterization technique. $^{35-37}$ Unfortunately, early attempts at measuring the element composition of III-nitrides materials using LAPT showed significant deviations from the correct values. Using LAPT on GaN specimens, different measurements observed a variation in Ga and N compositions as a function of laser pulse energy, voltage bias applied to the tip, and Ga^{++}/Ga^+ ratio, also called charge-state ratio (CSR).¹⁸⁻²⁷ Of all of the different approaches to analyzing and representing the compositional analysis of GaN, multiple research groups have recently settled on representing their results as a function of the Ga CSR.^{22,25,27} For many materials the CSR offers an indirect indication of the surface electric field strength across the tip apex according to the post-ionization theory of Kingham,³⁸ and is frequently a preferred parameter for the comparison of LAPT measurements of specimens of the same material studied under different experimental conditions and in different instruments.

In the literature, some measurements showed a linear increase in the Ga atomic fraction with increasing laser pulse energy (and decreasing tip field/Ga CSR), where the correct element compositional values were only obtained at very low laser pulse energies, others were able to measure the correct Ga atomic fraction at a specific crossover point when plotted against laser pulse energy or Ga CSR.^{20,22,24,26} Recent works presented a detailed study of elemental composition in GaN using different commercial LAPT instruments and specimen temperatures.^{25,27} These reports were able to measure the correct Ga and N concentrations for high Ga CSR (high field), but the Ga composition values diverged toward higher values for low Ga CSR. The reasoning given by the authors for this behavior is that low Ga CSRs reflect low-field/high laser energy pulse conditions which can result in N₂ neutrals formed by ion dissociation or unranged ion counts apparent in multiple hit events.^{39,40} Overall, all of these examples highlight how LAPT of GaN using conventional visible or NUV light sources is known to present significant compositional biases depending on the experimental parameters used in each experiment. For this reason, III-nitride materials have been labeled as model systems for the study of compositional biases in LAPT.²⁴

In this study, we use our EUV APT instrument to study multiple III-nitride samples, such as GaN, Mg-doped GaN, $In_xGa_{1-x}N$, and $Al_xGa_{1-x}N$. We specifically address whether a low-fluence EUV pulse, impinging on a needle-shaped compound semiconducting specimen under a high DC voltage bias, can trigger controlled field ion evaporation in these materials. Just as in the case of SiO₂,¹⁶ our results suggest the possibility for a different ion evaporation mechanism to the conventional thermal bulk heating process for these materials. Through measurements of the mass spectrum of these samples, we also assess whether this technique shows compositional biases similar to observations using other wavelengths and, in the case of doped samples, whether the doping measurement matches the concentration values obtained with other analytical techniques.

EXPERIMENTAL METHODS

The samples used in this study are a variety of III-nitride semiconductor materials: GaN, Mg-doped GaN, Al_xGa_{1-x}N, and In_xGa_{1-x}N. The GaN sample is a commercially available Ga-polar GaN-on-sapphire template. The unintentionally ndoped GaN layer is 5 μ m thick. The Mg-doped GaN was grown in-house using molecular beam epitaxy (MBE) on a GaN-on-sapphire template with the same specifications as for the GaN sample; for more details, refer to the Supporting Information (SI). The Al_xGa_{1-x}N ($x \approx 0.5$) alloy sample was grown using metal-organic chemical vapor deposition (MOCVD) and HVPE methods; a detailed description of the growth process was given by Sanford et al.⁴¹ The In_xGa_{1-x}N sample was grown by MOCVD at the University of New Mexico; specific details on the growth process can be found in the SI.

The specimens were prepared by standard focused ion beam (FIB) wedge liftout techniques, attached to the posts of Si transmission electron microscopy (TEM) half-grids, and sharpened into a needle-like shape by FIB annular milling.^{42–44} The final tip diameter for all of the specimens was in the range of 10–30 nm. The EUV atom probe instrument (Figure 1) used for these measurements has been described in detail by Chiaramonti et al.^{15,16} In summary, it consists of a Wyvern

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Figure 1. Schematic representation of the EUV APT instrument. A Ti:sapphire laser ($\lambda = 800 \text{ nm}$) is focused into an Ar-filled hollow-core waveguide for the generation of EUV light ($\lambda = 29.6 \text{ nm}$). The EUV beam travels inside a vacuum beamline designed to steer, monochromatize, and focus the EUV light into an ~50 μ m diameter spot at the specimen position inside the APT chamber.

laser system and XUUS EUV light source (KMLabs) coupled into a LEAP 3000X-Si atom probe chamber (CAMECA Instruments) by a custom-made vacuum beamline.^a The output of the ultrafast laser system is a 10 kHz train of pulses (1.2 mJ, 35 fs) centered at 800 nm. Inside the EUV light source, approximately 0.5 mJ of the 800 nm light is coaxially focused into an Argon-filled hollow-core waveguide for the upconversion into EUV light through the high-harmonic generation (HHG) process.⁴⁵⁻⁴⁷ Since the attenuation coefficient of EUV light in air is very high, the output of the EUV source is coupled to the atom probe chamber by a vacuum beamline. The main purpose of the vacuum beamline is to steer and focus the EUV light while also rejecting the residual co-propagating 800 nm light. Inside the atom probe chamber, the EUV light is polarized parallel to the long axis of the specimen, has a photon energy of 41.85 eV (λ = 29.6 nm) with a bandwidth of ~ 2.4 eV, an energy per pulse of ~ 0.5 pJ, and a pulse duration of ~ 10 fs. At the specimen location, the EUV beam is focused down to a spot with a diameter of \sim 50 μ m. The pressure inside the atom probe chamber was typically in the range of 3×10^{-9} Pa (2×10^{-11} Torr) to 7×10^{-9} Pa (5 $\times 10^{-11}$ Torr) and all of the specimens presented in this study were at a base temperature of 50 K.

It is worth mentioning that even though we use the electronic hardware and vacuum chamber of a commercial LEAP 3000 Atom Probe Instrument, our EUV APT system has a few experimental parameters that differ from a strictly commercial NUV LAPT system: (1) Our EUV APT system does not yet have automatic evaporation rate control. Specifically, at the start of a measurement, the DC voltage is selected to obtain evaporation rates above the background level. The DC voltage is kept constant, but as the specimen's tip starts to evaporate, the overall electric field at the tip decreases and so does the evaporation rate. The user must manually increase the bias voltage to increase the evaporation rate; there is no constant ion detection rate feature. For this reason, the electric field conditions in a long dataset can vary significantly, especially if the measurement was performed overnight without the presence of a user (see SI). (2) The repetition rate of the EUV pulsing system was 10 kHz. This is in comparison to commercial LAPT Instruments with typical repetition rates in the hundreds of kHz. (3) The energy per pulse at the specimen position was maximized and held constant at ~0.5 pJ. During the course of a run, the pulse energy can fluctuate up to ca. 20% and the pointing can drift, so it was checked periodically and adjusted. The EUV pulse energy is measured by inserting a Si photodiode in the path of the EUV beam to measure the EUV-induced current, from which we can calculate the EUV energy per pulse. We optimize the photodiode current by improving the coupling of the 800 nm laser beam into the hollow-core waveguide and by adjusting the Argon pressure inside the waveguide. While lower energies per pulse are achievable, performing measurements significantly below this energy per pulse value resulted in evaporation rates too low to be practical. This is distinct from commercial LAPT instruments which use sealed commercial laser systems that allow a range of pulse energies from fJ to nJ. (4) The EUV spot size at the specimen position is $\sim 50 \ \mu m$ in diameter, in comparison to the $\sim 2 \ \mu m$ spot size in some commercial systems. The larger EUV focus spot size and constant 0.5 pJ energy per pulse result in photon fluences that can be 2-5 orders of magnitude lower than what can be obtained with commercial LAPT instruments. As a result of all of these differences, the collected number of ions per dataset that we can measure with our current EUV APT system are on the order of 10^6 .

The analysis of our data was performed by a combination of commercially available software (CAMECA Instruments IVAS 3.8.0) and in-house developed programs. Mass calibrations, peak ranging, and composition measurements were automated using our in-house analysis software and were checked to be in reasonable agreement with IVAS-based analysis. In this work, a global background (i.e., flat background in time-of-flight space) was found to be sufficient and was used throughout all of the measurements presented in this manuscript. For peak ranging, the start and end limits were located at the position where the background-corrected counts had decreased to 10% of the peak maximum for each peak. For display purposes, mass spectra were computed using $1 \times 10^{-3} m/z$ bin widths and then a $30 \times 10^{-3} m/z$ smoothing filter was applied.^b The uncertainty values in the element composition analysis are given as the statistical uncertainties due to the Poisson noise in our data. Model uncertainty is discussed in the Supporting Information and refers to variations in the atomic percentage (atom %) of each element as the peak identification, peak ranging, and background subtraction are modified.

RESULTS AND DISCUSSION

Figure 2 shows the mass spectrum of a GaN specimen obtained with our EUV APT instrument. The DC applied bias was varied increasingly from 4.5 to 5.0 kV throughout the run and the number of ions detected for this dataset is on the order of 1×10^6 . As previously mentioned, all specimens were



Figure 2. EUV radiation-triggered mass spectrum of GaN (black) and time-independent global background (red). The EUV APT instrument experimental conditions were set at 0.5 pJ pulse energy, 41.85 eV photon energy, and 10 kHz repetition rate. The specimen's temperature was 50 K. The mass spectrum has not been background-corrected.

measured at a base temperature of 50 K, the EUV energy per pulse was ~0.5 pJ, and the repetition rate was 10 kHz. To our knowledge, this is the first report of EUV-assisted field ion evaporation from a semiconductor specimen. As with any atom probe mass spectrum, identifying and ranging the measured peaks are necessary to understand the specimen's elemental composition. The spectrum displays distinctive GaN features similar to the ones presented in other NUV LAPT studies. The Ga⁺ (68.9 and 70.9 m/z), Ga⁺⁺ (34.5 and 35.5 m/z), Ga⁺⁺⁺ (23 and 23.6 m/z), N⁺ (14 m/z), and N⁺⁺ (7 m/z) ionic peaks are clearly identifiable. Other peaks present in the mass spectrum result from complex-molecular ions such as N_2^+ (28 m/z), GaN⁺⁺ (41.5 and 42.5 m/z), and N₃⁺ (42 m/z). In comparison to NUV LAPT studies of GaN samples, this mass spectrum does not appear to show the presence of the complexmolecular ion GaN₃⁺⁺, typically present at 55.5 and 56.5 m/z_1 which is a distinctive feature in the visible and NUV mass spectra of GaN samples.^{18,21–23,26}

The identity of the peak at 14 m/z is debatable since it can correspond to singly ionized N atoms (N⁺) or to doubly ionized N molecules (N₂⁺⁺). We performed our data analysis under both scenarios, resulting in an overall variation of the N concentration of ~± 1 atom %. In this study, we identify the peak at 14 m/z as singly ionized N for all of the datasets and classify this small uncertainty as part of the model uncertainty. This identification is consistent with what has been observed for oxygen ions.^{48,49}

As previously described, in this dataset, we manually increased the DC bias in discrete steps to maintain an approximately constant evaporation rate. Following a step increase in the DC bias, the evaporation rate and Ga CSR would immediately increase. Then, during the subsequent hours, the evaporation rate and Ga CSR (Ga⁺⁺/Ga⁺) would slowly decay. Thus, during the 46 h that it took to obtain these data, the Ga CSR varies from 0.5 to 2.0. The overall average Ga CSR was 0.86, where the apparent Ga concentration is \sim 47.9 \pm 0.2 atom % and the apparent N concentration is \sim 52.1 \pm 0.2 atom %. To better understand the Ga and N compositional values for different Ga CSRs, we performed additional EUV APT GaN measurements, each containing ~4 \times 10⁵ ions, where the target average Ga CSR varied from 0.1 to 1. Figure 3a shows the overall apparent Ga concentration as a function of average Ga CSR for each of these measurements, while the individual EUV APT mass spectra are presented in the Supporting Information. To leverage these datasets to explore the maximum range of Ga CSR, we divide each dataset further during analysis. First, we segment the data based on ion sequence; this avoids averaging high- and low-field conditions together. In addition to segmenting the data based on ion sequence, we segment the data based on detector hit position. Previous work has shown that the Ga CSR may vary by at least a factor of five across a hit map with the highest Ga CSR located at the pole center.²⁷ Further, the same work noted that the composition vs Ga CSR data points generated by segmenting the data by detector hit position is consistent with the data obtained by changing the average surface field and averaging across the full detector. Thus, by segmenting our data points based on their distance from the pole center, we may explore a wider range of Ga CSR by simply not averaging out the known heterogeneity. More discussion of the segmentation is given in the Supporting Information.

Using this analysis procedure allowed us to plot the apparent Ga and N atom % over a large range of Ga CSR. Figure 3b



Figure 3. Apparent Ga concentration as a function of Ga charge-state ratio (Ga^{++}/Ga^{+}), where the dashed black line represents the nominal value of 50 atom %. (a) The different colors represent individual measurements performed under different field conditions; see the SI for more information and mass spectra for each dataset. (b) Segmentation of each dataset allows the analysis of the apparent Ga concentration for a larger range of Ga CSR. The error bars shown in (b) represent the counting statistics after segmentation of each dataset and are therefore larger than the error bars for each individual dataset.

shows the apparent Ga concentration as the Ga CSR varies from 0.03 to 6, where the dashed line represents the Ga stoichiometric value of 50 atom %. Overall, most data points lie within one to two sigma of the stoichiometric value; nonetheless, the apparent Ga concentration ranges from a maximum of 52.5 \pm 1.5 atom % to a minimum of 45.7 \pm 1.0 atom %. A notable feature from Figure 3 is that at Ga CSR above 0.5, we conceivably observe an underestimation of Ga. We expanded our data analysis and noted some detector multiplicity effects in the dataset with the highest average Ga CSR. When considering only single detection events, the apparent Ga concentration was 49.9 ± 0.3 atom %, while focusing on multiple detection events obtained an apparent Ga concentration of 47.2 ± 0.3 atom %. This effect is not as drastic in the lowest Ga CSR dataset where the apparent Ga concentration for single and multiple detection events was 50.4 \pm 0.3 and 49.7 \pm 0.3 atom %, respectively. This analysis suggests that multiplicity detection effects could be playing a role in the underestimation of Ga at high Ga CSR.

Our data differ from NUV LAPT $\tilde{G}aN$ reports that: (1) measure the correct stoichiometric value for a small range of Ga CSR, but overestimate the Ga content at low Ga CSR and underestimate it at high Ga CSR,^{22,26} or (2) observe the apparent Ga concentration starting to diverge from stoichiometric values for Ga CSR lower than ~0.2.^{25,27} We acknowledge that our data do not explore Ga CSR values lower than 0.03, but as previously mentioned this was due to the limitation in achievable EUV photon flux at the sample



Figure 4. (a) Schematic of the Mg-doped GaN sample. (b) EUV APT mass spectra of the Mg:GaN specimen (black), where the Mg⁺⁺ peak can be clearly resolved at 12 m/z. The data have not been background-corrected, and the time-independent background is shown in red. (c) SIMS measurements (red) and approximate specimen collection region (dashed green). The SIMS Mg concentration ranges between 2.5×10^{19} and 3.6×10^{19} cm⁻³ (uncertainty of ~±20%), in agreement with the EUV APT value of ~ 3.6×10^{19} cm⁻³. (d) Apparent Ga and N concentration as a function of Ga CSR. The dashed line represents a value of 50 atom %.

position. Future experiments with an instrument that allows for significantly higher pulse fluence will focus on exploring the behavior of the specimen's composition for lower Ga CSRs.

After verifying that controlled ion evaporation from undoped GaN samples is indeed possible with EUV light, our next effort focused on investigating whether EUV APT is capable of detecting the presence of minority species in p-type GaN samples. Figure 4a shows the schematic of an in-house MBE-grown sample with a 2.2 μ m top-layer of Mg-doped GaN, with an underlying 3.2 μ m undoped GaN layer on top of a sapphire substrate. The specimen used for the EUV APT measurement was collected at a depth of ~0.1 to 1.1 μ m with respect to the Mg:GaN surface. Figure 4b shows the EUV mass spectrum from such an Mg-doped GaN specimen. The peak identification is very similar to the one used in the GaN specimens, with the addition of the Mg⁺⁺ peak at 12 m/z. Using element compositional analysis, we obtain values of 49.2 \pm 0.2 atom % for Ga, 50.8 \pm 0.2 atom % for N, and 0.04 \pm 0.01 atom % for Mg, which results in a Mg concentration value of $\sim 3.6 \times 10^{19}$ cm⁻³. To verify if the EUV APT Mg concentration results are in the correct range, we performed secondary ion mass spectrometry (SIMS) on the sample from which the specimen was obtained. The SIMS measurements show that the Mg concentration ranges between 2.5×10^{19} and 3.6×10^{19} cm⁻³ depending on the specimen's depth. The SIMS Mg concentration results, shown in Figure 4c, have an uncertainty of $\sim 20\%$, but are within the value obtained by EUV APT. The analysis of the apparent Ga and N concentration as a function of Ga CSR is presented in Figure 4d. The data show the apparent Ga and N concentrations within one to two sigma of the expected value of \sim 50 atom % for the range of Ga CSR studied in this measurement. Our results suggest that the dopant has no significant effect on the concentration measurements. The limited number of counts in the Mg peak hindered the ability to study the Mg concentration as a function of Ga CSR.

After testing the analytical sensitivity of EUV APT on undoped and doped GaN samples, we focused our attention on the ternary semiconductor alloy $Al_xGa_{1-x}N$. For GaN, we know the element composition is fixed at 50:50; however, in $Al_xGa_{1-x}N$ alloys, the Al and Ga fractions are not perfectly known as variations can occur during the synthesis process. Exploring the behavior of such a sample with EUV APT is important because LAPT studies of Al_xGa_{1-x}N have shown conflicting results when measuring the Al atomic fraction as the field is varied.^{25,27,50–55} Additionally, even within the same study, the trends in the apparent Al concentration as a function of Ga CSR appear to depend on the Al concentration in the measured alloy.^{25,27,54} It has been proposed that part of the complexity in studying $Al_xGa_{1-x}N$ with LAPT derives from the fact that each element has a different evaporation field.³⁸ In $Al_{r}Ga_{1-r}N$, the underestimation of N is proposed to be, at low field/high laser pulse energy due to N₂ neutrals formed by molecular ion dissociation, and at high field/low laser pulse energy due to N evaporation in-between pulses, also called DC evaporation.²⁵ Some studies were not able to obtain accurate concentrations, independent of the field conditions,²⁵ while a subsequent report from the same group was able to attain the correct Al concentration values for a small tip-field range.² Other studies have measured the correct Al site fraction, but only under low-field conditions.^{53,54}

For our EUV APT measurements, we use an $Al_xGa_{1-x}N$ ($x \approx 0.5$) sample and verified the Al concentration values with energy-dispersive X-ray (EDX) spectroscopy. Figure 5a shows the mass spectrum ($\sim 7 \times 10^5$ ions) from our $Al_{0.5}Ga_{0.5}N$ specimen. The peak identification in this dataset is again very similar to the one in the GaN mass spectrum, with the addition of the Al⁺ (27 m/z), Al⁺⁺ (13.5 m/z), and Al⁺⁺⁺ (9 m/z) peaks. Additionally, the complex-molecular ion AlN⁺⁺ is clearly present at 20.5 m/z. Similar to the GaN analysis, by segmenting the data based on detector hit position and ion sequence, we are able to evaluate the elemental composition



Figure 5. (a) $Al_xGa_{1-x}N$ ($x \approx 0.5$) EUV APT mass spectrum (black) and time-independent background (red). (b) Apparent concentration for Al (yellow), Ga (blue), and N (green) as a function of Ga CSR. The dashed yellow and green lines represent the nominal values for Al (25 atom %) and N (50 atom %), respectively. The shaded yellow region represents the 25 ± 2 atom % Al concentration from the EDX measurement. The data show a continuous underestimation of N; see main text for further discussion. The error bars shown in this figure represent the counting statistics after segmentation of the full dataset and are therefore larger than the error bars for the full dataset.

for different Ga CSRs, as shown in Figure 5b. Our results show the average Al concentration value is 23.6 ± 0.1 atom %, well within the EDX value of 25 ± 2 atom %; however, the EUV APT data show a consistent underestimation of N and overestimation of Ga over the entire Ga CSR range. Therefore, our element composition analysis does not achieve the anticipated 50:50 ratio between N and (Al + Ga), contrary to our EUV APT results on GaN that show the Ga and N atom % close the stoichiometric values.

A detailed analysis of our data shows the apparent Al concentration, ranging between 22.6 \pm 0.9 and 24.8 \pm 0.8 atom %, remaining relatively uniform as the Ga CSR varies from 0.6 to 4. While these values are slightly below the expected concentration of 25 atom %, they are within the error of the EDX measurement, which measured an Al concentration of 25 \pm 2 atom %. In comparison, the Ga concentration, assumed to be ~25 atom %, is consistently overestimated as it ranges between 30.6 \pm 1.0 and 33.9 \pm 1.0 atom % and appears to decrease as the Ga CSR increases. Finally, our data show an underestimation of the apparent N concentration as it varies from 43.0 \pm 1.0 to 46.1 \pm 1.1 atom %, below the expected value of 50 atom %.

As previously mentioned, some reports interpret the underestimation of N, while at high-field/low pulse energy pubs.acs.org/JPCC

conditions, to be due to the DC evaporation of N.²⁵ This effect was implied from the rapid increase in the background signal as the DC voltage was increased. In our data, we do not observe such a strong increase in the background signal; therefore, it is unlikely that our N underestimation is caused by DC evaporation. The generation of N₂ neutrals by dissociation is another possibility, but in the correlation histogram (see the Supporting Information) the only notable dissociation curve is for $AlN^{++} \rightarrow Al^+ + N^+$.⁵⁶ The lack of other dissociation curves makes it unlikely that N2 neutrals from dissociation events are the main reason for the underestimation of N in our data. However, we do observe a significant difference in the apparent concentration results as a function of single or multiple detection events. When looking at only the single detection events, the apparent concentration values are $N = 40.3 \pm 0.2$ atom %, Ga = 39.3 ± 0.2 atom %, and Al = 20.4 ± 0.2 atom %. For multiple detection events, we obtain $N = 47.8 \pm 0.3$ atom %, Ga = 24.7 ± 0.2 atom %, and Al = 27.5 ± 0.2 atom %. This analysis shows a higher underestimation of N when filtering only single detection events, while filtering for multiple detection events yields an apparent concentration closer to the correct values. Given the significant difference between singles and multiples apparent concentrations it is possible that detector dead time is contributing to the underestimation of N.^{57,58} The data presented in Figure 5b are not filtered based on single and multiple detection events, but rather displays all detection events. Further explorations of this N underestimation behavior are necessary, where ideal experiments would include larger datasets, different Ga CSRs, and measurements on specimens containing different Al concentration values.

Another ternary system that has been carefully studied with LAPT is $In_xGa_{1-x}N$. In comparison to $Al_xGa_{1-x}N$ studies, some reports have been able to reliably measure the In concentration in $In_xGa_{1-x}N^{22,59}$ and $In_xAl_{1-x}N^{.22}$ For this effort, we use a sample with 4 nm thick $In_xGa_{1-x}N$ (x = 0.15) quantum wells (QWs) separated by 10 nm thick GaN barriers on top of a 65 nm thick n-doped $In_xGa_{1-x}N$ (x = 0.03) buffer layer. Figure 6a shows the TEM image of the sample used for EUV APT, including a representation of the needle-shaped specimen liftout, and the EUV APT mass spectrum for the Incontaining quantum well, GaN barrier, and In-containing buffer sections. Peak identification is similar to GaN with the additional peaks corresponding to In^+ (115 m/z) and In^{++} (57.5 m/z). The results of our element composition analysis for all of the different specimen sections and the specimen reconstruction are shown in Figure 6b. The low ion count in each section prevents the analysis of the apparent concentrations as a function of Ga CSR; thus, the results presented in Figure 6b are average values for each region. For this sample, SIMS and EDX measurements are not the appropriate characterization techniques because of the length scale of the QWs; therefore, we performed NUV LAPT measurements on a different specimen from the same sample to obtain the apparent In concentration in the various sections (see the Supporting Information for more details). The apparent In concentrations in the quantum well are 7.7 \pm 0.5 atom % with EUV APT and 7.3 \pm 0.4 atom % with NUV LAPT. Additionally, in the buffer section, the apparent In concentrations with EUV APT and NUV LAPT are 2.2 \pm 0.1 and 2.4 \pm 0.1 atom %, respectively. Our results with EUV and NUV LAPT are in agreement, therefore suggesting, similarly to previous reports using NUV LAPT,^{22,59} that EUV APT is able



Figure 6. (a) TEM image, EUV APT mass spectra (black), and time-independent background (red) of individual sections. The nominal layer compositions are labeled next to the TEM image, while the EUV APT mass spectra of the quantum well, barrier, and buffer sections are also shown. (b) EUV APT reconstruction of In and Ga atoms within the specimen and measured compositional analysis results for each specimen section.

to obtain the correct apparent In concentration values on the $In_xGa_{1-x}N$ alloy.

An important takeaway of our data is that EUV radiation pulsed atom probe tomography is indeed capable of triggering controlled field ion emission in an array of III-nitride semiconductor samples. However, it is vital to understand the photon fluence conditions and possible specimen temperature increase in our measurements. A detailed description of the following calculations was presented by Chiaramonti et al.¹⁶ In summary, the EUV energy per pulse impinging on the specimen is ~0.5 pJ and the $1/e^2$ beam diameter at the specimen's location is ~50 μ m. Using these values, we calculate the EUV fluence (energy per unit area) to be $\sim 5 \times$ 10^{-4} J/m². Additionally, we know the EUV photon energy is \sim 41.85 eV and we assume the specimen's needle apex to be a simple rectangle measuring 100 nm \times 100 nm in cross section. Thus, we estimate an average of one EUV photon per laser pulse incident on the specimen.

While it is difficult to imagine how one EUV photon can produce bulk heating, let us also calculate the maximum thermal energy that the EUV light pulse can impart to the specimen. The instantaneous temperature rise (ΔT) is defined as $\Delta T = E_A/(c\rho V)$, where the absorbed energy (E_A) is 5 ×

 10^{-18} J, the specific heat capacity of GaN at 50 K (c) is 0.5 J/ $(g \cdot K)$,⁶⁰ the density (ρ) is 6.2 g/cm³, and the relevant volume (V) is estimated to be 1×10^6 nm³. Using these values, we obtain a temperature rise of ~ 2 mK which strongly suggests the traditional model of field evaporation by absorption, bulk heating, and thermal cooling cannot be applied in this scenario. Additionally, we use Vegard's $law^{61,62}$ to extrapolate the $Al_xGa_{1-x}N$ ($In_xGa_{1-x}N$) alloy properties from the GaN and AlN (InN) endpoints. For $Al_xGa_{1-x}N$ (x = 0.5), we obtain a density of 4.7 g/cm³ and a heat capacity of 0.6 J/(g·K), while for $In_xGa_{1-x}N$ (x = 0.15), we get a density of 6.3 g/cm³ and a heat capacity of 0.5 $J/(g\cdot K)$. Since the density and heat capacity for the Al_xGa_{1-x}N and In_xGa_{1-x}N alloys are similar to those of GaN, the calculated temperature rise of these samples is also ~ 2 mK. Finally, using the same analysis, but assuming the use of an NUV LAPT instrument with an energy per pulse ranging from 5 fJ to 1 pJ and a focused spot size of 2 μ m,²⁵ the calculated temperature rise varies from ~ 10 mK to ~ 2 K.

The extremely low photon flux and temperature rise when using EUV light suggest that a different ionization and desorption pathway may be occurring on the samples presented in this work, just as the work with SiO_2 suggests. A careful examination of this EUV radiation-triggered field ion

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emission mechanism is beyond the scope of this manuscript and will be studied in future work. However, it is worth mentioning that it has previously been pointed out that even in NUV LAPT of GaN, the field evaporation behavior is not entirely consistent with a purely thermal model.⁶³

As mentioned in the Introduction, the fact that our EUV APT instrument was able to trigger controlled field ion emission from SiO₂ specimens did not imply that it would be successful on the III-nitride semiconductor samples presented in this study given the widely diverging material properties. When using NUV LAPT, the experimental conditions used on SiO₂ and GaN are significantly different, where SiO₂ samples are typically run at much higher laser pulse energies than GaN samples.^{20,22,25,64} However, all of the III-nitride samples presented in this study and our previously published SiO2 measurements were run with the exact same EUV pulse energy and repetition rate. The limitations of our current EUV APT instrument did not allow us to explore the large parameter space usually studied in conventional NUV LAPT. Nevertheless, we have been able to successfully run both semiconducting and insulating samples, and the apparent concentration values obtained in all of these samples, except for $Al_rGa_{1-r}N_r$ are close to the correct values.

The proof-of-principle measurements shown in this manuscript illustrate the potential of EUV light in the study of IIInitride semiconductors. However, as previously mentioned, our EUV APT instrument has some technological limitations that hinder our capabilities to deeply understand the ionization mechanisms involved in EUV APT. A careful comparison between EUV and visible/NUV APT requires an EUV APT instrument with increased photon fluence. Currently, we are in the process of upgrading our laser system and redesigning the vacuum beamline, with the goal of improving the photon fluence and data acquisition time. This will be accomplished by an increase in the laser repetition rate, a more efficient vacuum beamline, and tighter focusing conditions. When these modifications are performed, we will continue the exploration of using EUV APT on semiconductor samples.

CONCLUSIONS

In summary, we have shown that an atom probe tomograph that utilizes pulsed, coherent EUV light can successfully analyze an array of compound III-nitride semiconductor specimens. The low photon fluence conditions used for these measurements suggest that a different ionization mechanism to the traditional bulk heating model is occurring. When studying GaN specimens, our data show concentration results close to the stoichiometric values over a range of Ga charge-state ratios. Our concentration analysis results in the Mg-doped GaN specimen were in reasonable agreement with SIMS measurements. Our results on Al_xGa_{1-x}N samples obtained apparent Al concentration values within the error of the EDX measurements but show a consistent underestimation of N and overestimation of Ga as a function of Ga CSR. Further studies are necessary as we observe variations in apparent concentration values when focusing on single vs multiple detection events. Furthermore, our compositional analysis of the $In_xGa_{1-x}N$ QWs sample was able to obtain the correct concentration values for all of the different specimen sections. Finally, the results presented in this manuscript are a proof of principle that EUV APT can be applied to the study of compound semiconducting samples. Continued work will help to fully understand the benefits of EUV light pulses in the

development of LAPT for the field of semiconductor metrology.

ASSOCIATED CONTENT

③ Supporting Information

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The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c08753.

Sample preparation, uncertainty values, segmentation of datasets for charge-state ratio (CSR) analysis, $Al_xGa_{1-x}N$ data analysis, and $In_xGa_{1-x}N$ results with NUV LAPT (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the NIST Innovations in Measurement Science Program and material support from CAMECA Instruments through a cooperative research and development agreement. They kindly acknowledge J. Sheng for fruitful discussions and for performing the SIMS measurements.

ADDITIONAL NOTES

^{*a*}Commercial instruments, equipment, or materials are identified only to adequately specify certain procedures. In no case does such an identification imply recommendation or

endorsement by NIST, nor does it imply that the products identified are the best available for the purpose.

^bIn this manuscript, the conversion from SI units (kg/C) to the conventional mass-to-charge ratio (m/z) is implied.

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