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Impact statement Atomic layer annealing (ALA) presents the ability to enhance desirable properties of thin films deposited by atomic layer deposition processes, such as crystallinity, density, purity, and resistivity. ALA could also enable the deposition of materials typically grown by high-temperature processes at lower temperatures required for device integration. In this article, RF substrate-biased ALA is demonstrated as an effective means to deposit minimally contaminated and polycrystalline GaN films on insulating and amorphous substrates at 275°C. RF bias is required for deposition on insulating or patterned substrates to avoid charge damage. This method could be useful to deposit thin films of other group III-nitrides at low temperatures, such as AIN, InGaN, and AlGaN. Such materials are of interest to serve as heat spreaders, piezoelectric films, back-end thin-film transistors, and optoelectronic devices. These materials are typically deposited by metal-organic chemical vapor deposition at temperatures exceeding 800°C. Accordingly, lower-temperature deposition processes could enable their more widespread implementation in accelerating future technologies such as heterogenous integration, advanced packaging, and microLED displays.

## Atomic layer annealing with radio-frequency substrate bias for control of grain morphology in gallium nitride thin films

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A method of performing atomic layer annealing (ALA) with radio-frequency (RF) substrate bias on insulating and amorphous substrates is demonstrated for GaN deposition at 275°C. GaN is typically deposited by metal–organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE) at >600°C, resulting in strain upon cooling; this makes low-temperature process alternatives desirable. Tris(dimethylamido) gallium (III) and hydrazine served as precursors whereas Ar and Kr were used for ion bombardment. Optimization of substrate bias potential is demonstrated by grazing incidence x-ray diffraction (GI-XRD) and x-ray reflectivity (XRR). Reference films were deposited by thermal ALD and non-substrate-biased ALA processes. X-ray photoelectron spectroscopy (XPS) surface and depth-profiling studies show that applied RF bias decreases film oxygen and carbon content relative to the reference films; these films also show crystallites broadening with increasing film thickness by TEM in contrast to the reference films. In summary, ALA with RF substrate bias is demonstrated as an effective method to deposit GaN thin films at a low deposition temperature on insulators.

#### Introduction

Gallium nitride and other III–V materials are commonly deposited using high-temperature techniques, such as metal–organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) at temperatures exceeding 800°C.<sup>1–13</sup> These elevated temperatures are often necessary to promote reactivity of gaseous nitridation agents, such as ammonia or nitrogen/hydrogen mixtures, and to crystallize the deposited material. GaN is typically deposited on sapphire or silicon carbide substrates, commonly requiring thick aluminum nitride (AlN) buffer layers.<sup>3,5,6</sup> However, these elevated temperatures often produce stress in the films upon cooling due to differences in coefficients of thermal expansion.<sup>1,7,8</sup> Accordingly, lower-temperature deposition methods and post-deposition annealing treatments for III–V materials are a focus of the materials science community.<sup>14–17</sup>

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Plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PE-ALD) have shown promise for III-V materials; however, at low deposition temperatures compatible with standard techniques and equipment, PE-CVD and PE-ALD often produce films with high oxygen and carbon contamination.<sup>14,16,18–27</sup> Atomic layer annealing (ALA) processes have demonstrated an ability to further crystallize films deposited by both PE-ALD, where plasma-generated species serve as the co-reactant, and traditional thermal ALD with a chemical co-reactant.<sup>28-32</sup> In an ALA process, following each deposition cycle, a short bombardment with inert ions enhances surface adatom mobility and promotes the deposition of crystalline materials.<sup>28–33</sup> This allows for the healing of defects, such as amorphous chains on the growth surface and lattice vacancies on and below the growth surface. ALA processes may also produce films with comparatively lower contamination levels, as periodic ion bombardment could effectively heat the growth surface, thereby desorbing residual ligands and contaminants and could sputter surface-bound contaminants such as oxygen.<sup>28,31,32</sup>

Applying DC bias to conductive substrates during the ALA treatment allows the momentum of the bombarding ions to be controlled; this additional tuning ensures that sufficient momentum is transferred to atoms on the growth surface to heal defects while remaining under damage, implantation, and sputtering thresholds.<sup>31,32</sup> Similar observations have been made in PE-ALD processes with applied substrate bias.<sup>21,34,35</sup> The use of a substrate bias decouples the tuning of ion momentum from tuning of the ion flux, which primarily depends on the power applied to the plasma source. To date, ALA with substrate bias has been limited to DC bias applied; accordingly, development of ALA with RF substrate bias enables expansion of the ALA technique to insulating and patterned substrates without risk of damage due to charge buildup.<sup>31,32,36</sup> In the present study, RF substrate bias was applied during the ALA ion bombardment to deposit gallium nitride (GaN) on intrinsic silicon with 100 nm of thermal oxide (SiO<sub>2</sub>/Si) substrates.

GaN was chosen as a model system due to the potential of a low-temperature deposition method to produce polycrystalline thin films or crystalline material on lattice-matched substrates. Advances in low-temperature deposition on non-lattice-matched substrates could lead to widespread implementation of GaN in lower-cost applications.<sup>16,18,37</sup> GaN is a desirable material due to its large breakdown voltage and high mobility compared to silicon; it is utilized alongside InGaN in many photonic and optoelectronic devices and is of considerable interest to the microLED industry.<sup>9,38–44</sup>

#### **Results and discussion**

#### X-ray diffraction and x-ray reflectivity

Grazing incidence x-ray diffraction (GI-XRD) was used to quantify the crystallinity of the deposited thin films and x-ray reflectivity (XRR) was used to determine both density and thickness. All films deposited were of 30-35-nm thickness, except for those deposited at -44 V bias. A reference film deposited by thermal ALD was amorphous as determined by GI-XRD and had  $5.08 \text{ g/cm}^3$  density as determined by XRR. All films deposited by ALA, both with and without radiofrequency (RF) substrate bias, demonstrated diffraction at the expected (002) diffraction angle for gallium nitride (GaN). The GaN (002) diffraction regions for all films are shown in Figure 1; peak full width at half maximum (FWHM) and density by XRR are plotted as a function of substrate bias in Figure 2. In the reference depositions performed without RF bias applied, further denoted "ICP Only," a small -4 V self-bias is developed. For these inductively coupled plasma (ICP) only processes, both argon and krypton produced films with increased density relative to the thermal ALD reference film at 5.70 g/cm<sup>3</sup> and 5.62 g/cm<sup>3</sup>, respectively. These films demonstrated GaN (002) FWHM values of 0.76° and 1.02°, respectively, indicating a nanocrystalline morphology.

Applying RF bias to the substrates during each ion bombardment step further increased crystallinity, as is shown by a smaller GaN (002) FWHM, and increased density. At -14 V, films deposited using Ar and Kr bombardment show significant improvement over the ICP only processes: GaN (002) peak FWHM decrease to 0.57° and 0.65°, respectively, and film densities are closer to that of bulk GaN (6.15 g/ cm<sup>3</sup>) at 6.07 g/cm<sup>3</sup> and 6.09 g/cm<sup>3</sup>. Applying greater bias beyond -14 V shows only slightly increased density; this could indicate that at -14 V, the bombarding ions for both process gasses have sufficient momentum transfer to the growth surface to begin to heal defects such as vacancies and amorphous chains. These densities are greater than that reported by several PE-ALD techniques in the literature, ranging from 5.36 to 5.95 g/cm<sup>3</sup>, highlighting the ability of substrate-biased ALA to densify the material deposited by ALD.<sup>26,45</sup>

Film quality based on GaN (002) FWHM and density increase for the Ar and Kr processes at -24 V. The smallest GaN (002) FWHM of the Ar processes is observed at this condition 0.54 degrees. The density of this film is a bulk-like  $6.14 \text{ g/cm}^3$ . For the process run with Kr at -24 V, the (002) peak FWHM decreases to  $0.58^\circ$  and the density is slightly lower, at  $6.11 \text{ g/cm}^3$ . The optimal condition for Kr identified in this set is -34 V, where the film shows the most narrow (002) FWHM,  $0.51^\circ$ , and a bulk-like density of  $6.16 \text{ g/cm}^3$ . The variance between Ar and Kr in the bias at which optimal film quality is observed could be the result of differences in how the bombarding ions interact with the growth surface.

At -44 V, both Ar and Kr ALA processes show significantly increased (002) FWHM. Further, the thickness of these films deviated from that of films produced at all other conditions, decreasing to 24.3 and 27.3 nm, respectively; this could be the cause of the decreased peak intensity observed in Figure 1. These observations are consistent with the onset of sputtering by the bombarding ions.





**Figure 1.** Grazing incidence x-ray diffraction of all films. The GaN (002) diffraction peak region for each deposited film is shown. The thermal atomic layer deposition (ALD) process was only performed with Ar purge gas and shows that the film is amorphous. The ICP only processes deposited weakly polycrystalline films, while films deposited with applied radio-frequency bias demonstrate stronger crystallinity as indicated by the more narrow and more intense diffraction peaks. Note that the diffraction peaks are most narrow for the Ar –24 V and Kr –34 V conditions. Increasing the bias to the –44 V condition resulted in both decreased peak intensity and increased width, indicating that the ion bombardment was likely too energetic and began damaging the films.



**Figure 2.** Film quality as a function of substrate bias. The GaN (002) diffraction peak full width at half maximum (FWHM) determined by grazing incidence-x-ray diffraction and density determined by x-ray reflectivity fitting for the atomic layer annealed films deposited using Ar and Kr as the process gases. Both Ar and Kr showed similar initial results, with improvements in film quality at the –4 V (ICP only) process, and further improvements at –14 V. For the set of processe using Ar, optimal crystallinity was observed at –24 V, whereas Kr showed optimal crystallinity at –34 V. At –44 V, film quality degraded significantly, indicating the onset of sputtering and/or ion embedding.

#### Spectroscopic ellipsometry

The refractive indices of the films deposited using the Ar -34 V and Kr -34 V bias conditions were determined to be 2.133 and 2.318 at 633 nm, respectively. These results are comparable to those of polycrystalline GaN films deposited by both PE-ALD and PE-CVD.<sup>23,26,46-48</sup> The Kr -34 V process result is within 3% of that of bulk GaN at 2.385 and is competitive with reported values for MOCVD processes, ranging from 2.24 to 2.397.<sup>49-51</sup>

#### X-ray photoelectron spectroscopy

Composition of the films produced by the thermal ALD process, the ICP only processes, and the conditions at which Ar and Kr showed optimal crystallinity are shown in Figure 3. This composition information was determined by x-ray photoelectron spectroscopy (XPS) with corresponding photoelectron spectra and peak fits shown in Supplementary information Figure S1. It is noted that although films do not show 1:1 Ga:N stoichiometry, the films may be stoichiometric, as the large difference in binding energies between the Ga 3d region and N 1s regions at 19 eV and 397 eV, respectively, could result in varied photoelectron yield that is not entirely accounted for by the Scofield relative sensitivity factors utilized in calculating film composition. The thermal ALD film demonstrates the greatest oxygen content of 1.7 at.%. Atomic layer annealing reduces this contamination in all cases, with the largest oxygen reductions observed upon applying additional RF substrate bias to 0.4% and 0.7% for the Ar and Kr processes, respectively. This is consistent with ion bombardment resulting in the preferential sputtering of contaminants, such as residual ligands, and light elements, such as oxygen and carbon, from the growth surface during deposition. These results are a significant improvement over some of the lowest reported oxygen content of 1-2 at.% in the PE-ALD literature.<sup>26,28</sup> Due to the presence of multiple features in the C 1s region, carbon content was not analyzed in these experiments; however, carbon KLL Auger signal was not observed in any initial XPS survey scans.

#### Depth-profiling x-ray photoelectron spectroscopy

The depth-dependent composition of an additional film deposited on  $SiO_2$  using the Ar -14 V condition is shown in **Figure 4**, as determined by depth-profiling XPS. Due to the exposure of the sample to atmosphere prior to characterization, the surface of the film oxidized to approximately 9.2% O.



**Figure 3.** Film composition determined by x-ray photoelectron spectroscopy. The composition of the top 3-5 nm of films produced by the reference thermal annealing layer deposition (ALD) process, the reference Ar and Kr ICP only processes, and the optimal Ar -24 V and Kr -34 V processes. Note that all atomic layer annealing conditions show decreased oxygen content relative to the thermal ALD film, with greatest reduction observed on both samples with applied radio-frequency bias. Note that 1:1 Ga:N stoichiometry is not observed; however, this could be an effect of the large differences in binding energies between the Ga 3d and N 1s photoelectron-binding energies.



**Figure 4.** Film composition by depth-profiling x-ray photoelectron spectroscopy. A GaN thin film deposited using the radio-frequencybiased Ar -14 V condition on a SiO<sub>2</sub> substrate shows an oxidized surface due to atmospheric exposure before analysis and a relatively pure bulk region with average 48.4% Ga, 49.6% N, 1.8% O, and 0.2% C contents.

The surface oxidation reduced to the baseline level of oxygen detected in the film after eight etching steps. The bulk of the film has an average composition of 48.4% Ga, 49.6% N, 1.8% O, and 0.2% C. The higher observed oxygen content in the bulk of the film relative to the *in vacuo* XPS performed immediately after sample deposition could be due to edge effects, as the 2-mm width of the sputtered region is close to the 2.5-mm width of the substrate coupon. These discrepancies could also be due to differences in fitting procedure and sensitivity factors for the two XPS instruments. The low carbon content in the bulk of the film is consistent with ion bombardment promoting desorption of residual ligands and contaminants from the growth surface during each ALA cycle. It is possible that ALA with further increased substrate bias potential, such

as the optimal -24 V and -34 V conditions, could demonstrate lower bulk oxygen content due to increased kinetic energy of the bombarding ions sputtering contaminants from the growth surface.

### Transmission electron microscopy analysis

The transmission electron microscopy (TEM) and accompanying fast Fourier transform (FFT) analysis for a film deposited by each of the ICP only, -24 V, and -34 V conditions with Ar and Kr are shown in **Figure 5**.

Copies of all micrographs with polycrystalline grains outlined and enlarged FFT patterns are shown in Figures S2-S7. The ICP only films deposited using Ar and Kr, 5a and 5d, respectively, demonstrate an amorphous region nearest to the substrate interface identified by the presence of rings rather than discrete diffraction spots in the FFT analysis region I. A morphology of packed crystallites develops with increasing film thickness as shown by the presence of arcs in the FFT analyses for regions II-IV. Notable is the absence of any progressive strengthening of diffraction spots with film thickness; this indicates that film is composed of packed nanocrystalline regions without preferred orientation. This could be due to the bombarding ions having kinetic energy sufficient to increase local surface adatom mobility leading to the creation of nanocrystalline regions, but insufficient to facilitate the development of long-range order. This is consistent with the large GaN (002) FWHM and low density of these films as identified by GI-XRD and XRR (Figures 1 and 2).

The -24 V conditions for Ar and Kr, 5b and 5e, respectively, show an amorphous layer similar to that of the ICP only conditions at the interface; however, in these films, crystallinity increases with further deposition. This is observed by the broadening of crystalline regions with increasing film thickness in the micrographs and gradual strengthening of diffraction spots in the FFT patterns from regions II to regions IV. Of note is the significant tilting of grains in the Kr -24 V film, which is visible in the TEM and in the orientation of the FFT patterns. This tilting could have produced a broadened (002) diffraction peak in GI-XRD, as indicated in Figures 2 and 3.

The micrographs are shown in Figures 5c, f for -34 V conditions for Ar and Kr. These films demonstrate morphologies and increases in crystallinity with thickness similar to the films deposited at -24 V, which is consistent with only minute differences identified by GI-XRD and XRR. The ability of





the -24 V and -34 V ALA deposition processes to facilitate long-range order indicates that increased kinetic energy of the bombarding ions could induce collision cascades capable of healing subsurface defects during the growth process. It is also possible that the increased kinetic energy could be responsible for sputtering any oxygen from the growth surface, leading to the lower oxygen content as detected by XPS (Figure 3).

#### Conclusion

The present results demonstrate the ability to perform RF substrate-biased atomic layer annealing on amorphous and insulating substrates to deposit polycrystalline GaN of greater quality than reference depositions performed by thermal ALD or ALA without applied substrate bias. The optimization of bias potential is necessary to ensure that the kinetic energy of the bombarding ions remains below sputtering and implanting thresholds. The GI-XRD and XRR results demonstrate marked increases in film density and decreases in diffraction peak width at moderate -24 V and -34 V biases with ion bombardment by Ar and Kr. The *in vacuo* XPS composition analysis demonstrates that applied substrate bias in an ALA process can improve film composition by reducing oxygen content. Comparison of

films deposited by the -24 V and -34 V RF-biased ALA conditions using TEM and FFT analysis demonstrates that while ALA without substrate bias can deposit polycrystalline films, an applied RF bias enables the development of long-range order in the deposited material. In comparison to previous DC-biased ALA studies of aluminum nitride, with this RF-biased study, minimal difference exists in the morphology of films deposited using Ar and Kr plasma treatment. This technique could find use in the deposition of high-quality polycrystalline thin films at low temperatures on amorphous and insulating materials commonly utilized in optoelectronics, back-end thin-film transistors, and metal semi-damascene deposition processes.

#### **Materials and methods**

#### Substrates and handling

Silicon (100) wafers with a 100-nm-thick thermal oxide layer  $(SiO_2/Si)$  were purchased from University Wafer, Inc. Substrate coupons were diced, degreased using 30 s rinses of acetone, methanol, and water, and dried under N<sub>2</sub> before insertion into a load-lock vacuum chamber attached to the deposition and analysis chambers.



#### ALA vacuum chamber

ALA was performed in a homebuilt vacuum chamber system with a remote ICP plasma source (PIE Scientific Semi-KLEEN Sapphire Plasma Cleaner) and a homebuilt radio-frequencybiased stage assembly. The stage was heated by an embedded cartridge heater controlled by a variable AC transformer such that the substrates in the sample carrier were heated to 275°C, as determined by prior calibration studies. This chamber was pumped by a turbomolecular pump (Pfeiffer HiPace 300P). The walls of the ALA chamber were heated to 90°C while all tubing leading to the turbomolecular pump was not heated; an inline liquid nitrogen trap (A&N Corp.) was filled approximately 20 min before each deposition to condense trace contaminants out of the gas phase. This resulted in a base pressure of  $8 \times 10^{-7}$  Torr.

#### Precursors, dosing, and plasma treatment

Tris(dimethylamido) gallium (III) (TDMAGa, STREM Chemicals) was heated to 110°C for deposition and held at 90°C for storage; the dosing line was constantly heated to 115°C. Anhydrous hydrazine was supplied by RASIRC, Inc. and neither the precursor bottle nor the dosing lines were heated. Accordingly, the reported ALA technique is based on a thermal ALD process rather than a PE-ALD process. Argon push gas was used for both precursors and was purified using an Entegris GateKeeper placed just before the precursor containers. All precursor dosing and plasma treatment, a schematic of which is shown in **Figure 6**, was controlled by a LabView program. Each dosing cycle consisted of a 200 ms TDMAGa pulse (~40 mTorr) and a 175 ms hydrazine pulse (~60 mTorr) followed by purge times of 3 s and 7 s, respectively.

Approximately 7 sccm of Ar (PraxxAir 99.99%) or Kr (AirGas, 99.99%) was flowed through the vacuum chamber throughout the entire deposition, meaning this gas serves as both purge gas during precursor dosing and as the source of ions for plasma treatment. This brought the background pressure to 6 mTorr. To strike a plasma in the downstream ICP source (25 W, 13.560 MHz), an additional 20 sccm of gas was introduced for 1.5 s, briefly increasing the chamber pressure to 12 mTorr. An additional 500 ms long pulse of the desired ALA treatment gas at 80 sccm was used to extend the plasma into the deposition chamber. Following return to the background pressure of 6 mTorr, radio frequency bias was applied to the substrates for 8 s; this bias was supplied by an RF power supply (Manitou Systems Inc., 13.555 MHz) with the applied power adjusted to produce the desired substrate bias as indicated by the power supply display. All depositions were performed for 300 cycles.

#### **Deposition of reference samples**

An ALD reference sample was deposited, where each cycle consisted of steps I–V from Figure 6. ALA reference samples without an applied substrate bias were also deposited, with each cycle consisting of steps I–IX in Figure 6. Ions generated by the ICP source produced a small self-bias of -4 V for both Ar and Kr.

#### X-ray diffraction and x-ray reflectivity

Grazing incidence x-ray diffraction (GI-XRD) and x-ray reflectivity (XRR) measurements were performed on a Rigaku SmartLab system with a Cu anode operating at 2 kW under parallel beam configuration. GI-XRD measurements were performed using an incidence angle of 1.005° over a range



Figure 6. Precursor pulsing, purging, and plasma treatment schematic. Each atomic layer annealing cycle consisted of the following steps: I. Either Ar or Kr served as both purge gas and as the plasma treatment gas. II. TDMAGa pulses were 200 ms in duration and approximately 40 mTorr, followed by a 3 s purge (III). IV. A 175 ms pulse of hydrazine increased the chamber pressure to approximately 60 mTorr and was followed by a 7 s purge (V). VI. Additional gas required to strike a plasma in the remote ICP source was introduced, which brought the chamber pressure to 12 mTorr. VII. The plasma was contained in the remote ICP source until a larger pulse of gas extended the plasma into the deposition chamber (IX). X. Upon pumping down to the constant 6 mTorr purge pressure, radio-frequency (RF) bias (if utilized) was applied to the substrates for 8 s.



25–45° 2 $\theta$ ; diffraction peaks were analyzed using Rigaku GlobalFit software. XRR profiles were obtained over 0–4° 2 $\theta$  and were modeled to an R<sup>2</sup> value of less than 0.02 using Rigaku GlobalFit software to determine film thickness and density.

#### Spectroscopic ellipsometry

Spectroscopic ellipsometry was performed using a J.A. Woollam M-2000D instrument at 500 wavelengths across a 193–1000-nm range and at a 75° incidence angle. The data were modeled using CompleteEASE software with an SiO<sub>2</sub> layer of 100-nm thickness and a GaN layer of thickness equivalent to that determined by XRR. The fit refractive index, n, of the films is reported at 633 nm.

## Analytical vacuum chamber and x-ray photoelectron spectroscopy

Following deposition, each set of samples was transferred without vacuum break to a separate chamber (Omicron VT) containing an x-ray photoelectron spectroscopy (XPS) system (STAIB Instruments DESA 150 CMA, Mg Ka source 1253.6 eV). A combination of turbomolecular, ionization, and titanium sublimation pumps utilized in this chamber maintained a base pressure of  $5 \times 10^{-10}$  Torr. Photoelectron spectra of the Ga 3d, N 1s, and O 1s regions were recorded at a 45° collection angle. Composition of the films was determined by peak fitting in Casa/XPS 2.3 software using Shirley background profiles and correction using Scofield relative sensitivity factors.

#### Depth-profiling x-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) with depth profiling was performed on a film deposited using the Ar -14 V RF-biased ALA condition. Due to technical difficulties, this film was deposited with chamber pumping performed by a turbomolecular pump with an integrated Holweck backing stage (Edwards EPX 500 NE). This required minor adjustments to precursor pulse lengths and gas flow rates to maintain equivalent dosing and plasma treatment pressures. The spectroscopy was performed in a Thermo Fisher Scientific Nexsa Surface Analyzer XPS instrument and was analyzed using Thermo Fisher Scientific Avantage (version 5.9925) software at Wayne State University. Sputtering was performed over a 2 mm × 2 mm area using argon ions supplied by an argon sputter gun positioned at a 45° angle with respect to the substrate normal. Incremental sputtering was performed in 30 s etch intervals with 500 eV acceleration potential. Measurements were made over a 0.2 mm<sup>2</sup> area using an Al Ka (1486.6 eV) x-ray source at a chamber base pressure of  $10^{-8}$  Torr. High-resolution photoelectron spectra were collected for the Ga 2p, N 1s, O 1s, C 1s, and Si 2s ionization regions. Shirley background fitting was used in fitting peak areas from the high-resolution scans. The etching and characterization were performed for a total of 60 increments.

#### TEM

Lamellae from selected films were prepared by Eurofins EAG (Sunnyvale, Calif.) with final thinning to approximately 30 nm. TEM was performed on a Thermo Fisher Talos F200X instrument at 200 kV acceleration in bright-field configuration. Image acquisition was performed using a Ceta 4 k  $\times$  4 k CMOS camera and Velox software. FFT and image processing were performed using Gatan Microscopy Suite software.

#### **Author contributions**

A.J.M. and P.C.L. performed sample deposition, characterization, and analysis by XRD, XRR, XPS, and TEM. A.J.M. and S.T.U. constructed the vacuum chamber apparatus for the depositions and XPS analysis, and performed preliminary experiments. A.J.M. prepared the manuscript with guidance from all authors. Z.J.D. and C. Winter performed the depth-profiling XPS and provided related analysis and interpertation. J.S. provided technical guidance on the hydrazine source. R.K. and M.M. provided technical guidance on the tris(dimethylamido) gallium precursor. A.C.K. directed the study and assisted in manuscript preparation and editing.

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#### **Data availability**

The authors will freely provide all raw data upon reasonable request.

#### **Conflict of interest**

The authors declare no competing conflicts of interest. The hydrazine and tris(dimethylamido) gallium precursors were supplied by RASRIC, Inc. and EMD, respectively.

#### Supplementary information

The online version contains supplementary material available at https://doi.org/10.1557/s43577-023-00539-y.

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