It is shown that attractive electrostatic interactions between regions of positive charge in RF plasmas and the negative charge of metal wetting layers, present during compound semiconductor film growth, can have a greater influence than substrate temperature on film morphology. Using GaN and InN film growth as examples, the DC field component of a remote RF plasma is demonstrated to electrostatically affect metal wetting layers to the point of actually determining the mode of film growth. Examples of enhanced self-seeded nanopillar growth are provided in the case where the substrate is directly exposed to the DC field generated by the plasma. In another case, we show that electrostatic shielding of the DC field from the substrate can result in the growth of Ga-face GaN layers from gallium metal wetting layers at 490 °C with root-mean-square roughness values as low as 0.6 nm. This study has been carried out using a migration enhanced deposition technique with pulsed delivery of the metal precursor allowing the identification of metal wetting layers versus metal droplets as a function of the quantity of metal source delivered per cycle. It is also shown that electrostatic interactions with the plasma can affect metal rich growth limits, causing metal droplet formation for lower metal flux than would otherwise occur. Accordingly, film growth rates can be increased when shielding the substrate from the positive charge region of the plasma. For the example shown here, growth rates were more than doubled using a shielding grid. Published by AIP Publishing.

I. INTRODUCTION

Electric fields have been used for film growth over many decades; in particular, liquid phase epitaxy (LPE) techniques, called electroepitaxy, have been developed. For that situation, the field is applied directly across an electrically conducting melt. The control of ions by electric fields, through capacitively coupled electrostatics, across a vacuum, or across a plasma environment, is also well known and embodied in standard physics texts. However, other aspects of electrostatics during film growth are largely unreported. Li et al. mentioned the alignment of In₂O₃ nanopillars in the electric field of a plasma environment. Others have noted the alignment of carbon nanotubes in the electric fields created by plasmas. In those papers, the authors only noted the alignment of nanopillars in an electric field. In this paper, we describe the influence that electric fields have on metal wetting layers, sometimes referred to as adatom layers, showing that a previously unidentified mechanism of nanopillar growth can be initiated or suppressed by electrostatics related to the plasma environment. Further to this, we show that film growth rates can be severely limited by electrostatic interactions between the positive charge regions of an RF plasma and the negative charge of a metal wetting layer.

For the current experiments, a deposition technique with pulsed metalorganic delivery, “MEAglow” (Migration Enhanced Afterglow), has been used to help identify the physical processes that resulted from the use of an RF plasma source operating at 13.56 MHz. In particular, we examined the case of GaN film growth for which there has been some past characterisation of metal adatom species on the surface. We also provide some InN data, which show that these results are more broadly applicable.

II. EXPERIMENTAL

For the current experiments, the MEAglow growth technique with pulsed metal precursor delivery has been used to help identify the physical processes that resulted from equipment changes; further details of film growth not found here can be found in the references cited. During this pulsed deposition, a metal layer is deposited and then subsequently nitrided with a nitrogen plasma to form a group III nitride semiconductor layer. The metal deposition step is
critical to the deposition process. Uniquely, pulsed metal precursor delivery allows some evaluation of the morphology of the metal adatom layer that may not be as easily observed with continuous film growth. For instance, the film surface roughness, as a function of the amount of metal deposited per cycle, can be used to determine the presence or absence of a metal wetting layer.

The deposition per cycle was calculated here by total film thickness divided by number of deposition cycles. This calculation ignores any time events related to the initial nucleation on the c-plane sapphire substrates used, but as the films are relatively thick with many cycles used, the error is minimised.

The MEAglow technique is a CVD growth method, used at a relatively low pressure (for CVD) of typically 1–3 Torr. A hollow cathode nitrogen plasma source was used to supply active nitrogen species during film growth. For the experiments described here, trimethylgallium (TMG) and trimethylindium (TMI) were used as metal precursors for the growth of GaN and InN, respectively, and the film growth was carried out on c-plane sapphire substrates. Nitrogen flow rates from the plasma source were between 700 and 2000 sccm.

Before loading the substrates in the film growth chamber, they were cleaned with solvents and then they were heated to 1050°C in air for an hour and cooled over many hours. This procedure removed absorbates, but also reduced the surface damage caused by electromechanical etching of the substrate by the manufacturer, and is similar to that outlined by Cui et al. After loading in the growth chamber, the sapphire substrates were subjected to 1 min of nitridation with a nitrogen flow rate of 1000 sccm and a plasma power of 100 W. It was found that this level of nitridation was enough to convert the sapphire surface to a nitride but did not result in the pillar formation that can occur when excess nitridation is applied.

It should be noted that for actual film growth the plasma was on continuously at 600 W of power in a metal modulated epitaxy like experiment. However, unlike the case of metal modulated epitaxy (described for use at lower pressure using molecular beam epitaxy (MBE)) in the case of MEAglow, during the introduction of metalorganic the active nitrogen species do not reach the substrate because of gas phase interactions with the metalorganic. The delivery of active nitrogen species was therefore modulated since active nitrogen species were only delivered in the absence of the metalorganic.

It should further be noted that the nitrogen plasma was in a remote plasma configuration for these experiments, so that the flux of more damaging species (such as ions and higher energy radicals) reaching the substrate was minimised.

A cross-sectional schematic diagram of the growth system is shown in Figure 1. Film growth experiments were carried out with grids in the three positions, A, B, and C shown in the figure. That is, with biased or grounded metal grids placed between the plasma source and substrate pedestal at those three positions. The substrate holder was 10 cm in diameter, made of molybdenum, and was grounded. When in place, grid A was directly in front of the plasma source (see Figure 1). This grid had 1.45 mm holes with a 2.4 mm pitch between holes set out in a hexagonal packing pattern. When in place, grid B was set 30 mm below grid A and also grounded. Grid B had 69 × 8 mm diameter holes offset from the holes of the hollow cathode; it was largely in place to limit the energy of the plasma species through gas collision. When in place grid C was set 40 mm above the substrate holder, this grid could be grounded or independently biased. It was a stainless steel mesh with 1 mm diameter wire with a 5 mm pitch. The substrate holder to plasma source distance was 125 mm.

Films were characterised by surface imaging and surface roughness measurements collected using a Nanosurf easyScan 2 atomic force microscope (AFM) in ambient atmosphere. A SU-70 analytical ultra-high resolution scanning electron microscope (SEM) was used to determine the thickness of the layers (in cross section) and, to augment the AFM surface scan information, surface scans were also taken with the SEM. In some cases, where the films were too insulating, too thin or too rough to obtain a thickness from SEM cross-sections, film thickness was determined by UV-Vis optical transmission measurements using a Cary 5E spectrophotometer from which the film thickness can be found from optical interference fringes. A standard GaN refractive index of 2.45 was used, ignoring wavelength dependent variations. For some of the more gallium rich films, we found that this could overestimate the thickness by as much as 30% compared to SEM measurements, probably as a result of refractive index variation from the value used. X-ray diffraction ω-2θ scans were carried out using a PANalytical X’Pert Pro MRD diffractometer. Some characterisation of the plasma source is also provided.

It can be appreciated that no buffer layers were used during the film growths reported here. Growth was directly on the sapphire substrate. Bulk properties could undoubtedly...
be improved using standard buffer layers but would have unnecessarily complicated the determination of film thickness. It is the surface properties of the films that are of interest here.

III. RESULTS

A. Plasma source and grid considerations

There is considerable familiarity with the use of grids in conjunction with plasmas for ion flux control. That is, for the control of ion currents, however, that is not what is being examined in this paper. Rather than ion currents we are concerned here with the electric field or potential generated by the plasma and its interactions with films. A remote plasma was therefore used for the experiments conducted here. Ideally, we would prefer zero ion current to be present near the substrate during growth for all the cases mentioned below; however, in the practical circumstances of film growth with plasmas, this is not completely possible. Also, as mentioned in Section IV, some non-plasma vacuum based experiments have already been carried out for metal ion sources and can be related to these results. Regardless of that, it is useful in this circumstance to have a more accurate picture of what exactly a “remote” plasma entails.

For a hollow cathode plasma source, such as that used here, an ion rich plasma sheath forms near the metal surfaces of the cathode, and any ground plains that the plasma may be in contact with. The plasma itself acts as a virtual anode. The ion sheath has a positive potential because ions are too large to react to the RF field, while the smaller electrons can react, the ions therefore segregate in the RF field creating a DC potential. For an inductively coupled plasma source operating in the same frequency range, a similar positive potential occurs with an ion skin developing, though this “skin” is thicker than a plasma sheath.

Using the methodology described elsewhere, we have used a Langmuir probe to measure electron density near the hollow cathode without any of the grids in place. It was not possible to measure this in a cathode hole, as the probe quickly overheated there; however, we were able to take measurements in the sheath that extended from the front face of our hollow cathode plasma source. A value of $7.8 \times 10^{11}$ electrons/cm$^3$ was observed at a nitrogen pressure of 1.6 Torr. This pressure was typical of that used in our growth experiments. Only 7.5 mm below this position (the exposed probe tip was 3 mm in length) the electron density dropped to $0.32 \times 10^{11}$ electrons/cm$^3$ or approximately one twentieth of the value found closer to the cathode face. Assuming a Maxwellian plasma, our electron density should drop exponentially from the face of the plasma source due to gas collision. This means that at the position of grid B (approximately 27.5 mm lower than the initial measurement) the electron density would only be around $6 \times 10^9$ electrons/cm$^3$ and at the substrate position the electron density would be negligible. This suggests that indeed the ion flux should have very little influence on the experiments described here with only neutral radicals being used for film growth.

The plasma generation in the holes of a hollow cathode source should be close to a Maxwellian distribution with a fairly low energy distribution as these sources are known for extremely efficient production of radicals with ionisation occurring at very low bias voltages between the metal hollow cathode and the plasma sheath. As previously reported, optical emission spectroscopy results often show no ion peaks when looking directly at the plasma source as the signal from the ions is overwhelmed by radical production. However, this hollow cathode was also capacitively coupled to the grounded walls of the chamber with a plasma occurring there; in that instance, a DC bias potential of tens of volts was generated so that a small flux of ions near those energies could be expected. We have not attempted Langmuir probe measurements for these species further away from the plasma source as these higher energy ions would be non-Maxwellian and are likely to be present in greater proportion further from the plasma source so that any electron density measurements with a Langmuir probe would not be valid. It can be seen that the electron saturation region of the lower current measurements in Figure 2 (at the higher positive voltages) shows a very non-Maxwellian distribution, possibly a bi-Maxwellian distribution with one distribution (at $>50$ V) possibly due to the capacitive coupling to ground, though overall the electron saturation region is also affected by gas collisions at this relatively high pressure.

The plasma potential for the measurements of Figure 2 cannot be determined accurately because of the RF nature of the field which adversely affects the time averaged electron saturation region, the floating potential, and the plasma potential. However, it can be seen that the potentials are shifting to more positive values further from the plasma generation region. This shows that the region downstream of the plasma is the equivalent of a plasma “skin.” It is removed from the ion sheath near the metal surface of the hollow cathode; however, because the ions travel further than the electrons from the plasma generation region, the floating potential becomes more strongly positive.

The measurements of potential given further from the plasma, at 40 mm above the substrate, were just the floating potential for the probes used. Because the ions are not
strongly reactive to the RF field, and because the RF field is largely absorbed in the plasma environment, in that remote downstream region the RF is strongly masked with mainly the DC potential of the ion skin influencing the measurement there. The situation for an ICP source in a remote configuration would be similar.

In terms of the samples, any residual RF field reaching there would not be expected to have an influence on the migration of species, as space-charge polarisation (related to the movement of ions in a solid) occurs at much lower frequencies. This is equivalent to the situation for ions in a RF plasma. A plasma generated by RF power will also have a natural frequency of operation that can be some hundreds of kilohertz, but this is also too high a frequency to influence the effects described here. The DC component of the plasma is the main potential of interest.

In the absence of ions, the probe above the substrate would in fact be measuring the potential due to the induced electric field alone. So if the probe were one third of the distance between ground and a positive potential of 100 V, it would measure 33 V. However, as we expect a small flux of ions with energy of some tens of eV could potentially be present, the media between the plasma generation site and the probe is somewhat leaky. Therefore, the floating potential measured at the probe will tend toward that of the plasma potential of the plasma skin. It should be noted that some of the authors have examined the energy distribution of the ion species generated from a hollow cathode operated under DC conditions and may present those results separately.

For case (3) below, it is noted that the application of a negative potential on the grid could attract ions toward the grid, though their travel would be retarded beyond the grid toward the substrate. The applied voltages (tens of volts) are also quite low compared to those usually used for ion extraction (hundreds of volts).

**B. Case (1) +78 V DC potential, grid B only in place**

With only grid B in place, and the plasma source operated at 600 W of 13.56 MHz power, a floating DC potential of +78 V was observed at 4 cm above the sample holder. As explained above, this DC potential was present because a RF plasma in this frequency range becomes a virtual anode. Electrons are able to react to the RF field, whereas the heavier ions are less able to do so. The net effect is that 13.56 MHz RF plasma sources generate a positive DC potential at their periphery. This potential can extend beyond the range of ions related to the plasma.

In this case, the grounded grid B with large 8 mm holes was insufficient to shield the substrate area from the potential generated by the plasma. Under these conditions, we grew GaN and InN layers on the c-plane sapphire substrates, the substrates being highly insulating, and the growth front of the GaN and InN was therefore exposed to the +78 V potential.

Using MEAglow deposition with pulsed metal precursor delivery, samples were grown using a fixed amount of metal deposition per cycle over a number of cycles. The cumulative effect could then be analysed. The surface structure diagram, Figure 1(a) of Heying et al., recreated here in Figure 3, is instructive in relation to this. The diagram shows three regimes for the growth of GaN related to the Ga flux of MBE growth: the nitrogen stable regime, which is for nitrogen rich growth, and the two gallium rich regimes, the so-called intermediate regime and the gallium droplet regime. More recently, there has been further division of the gallium rich intermediate regime (by the same group as Heying et al.) to include a so called layer by layer regime for the situation where the gallium adlayer is less than or equal to a monolayer.

The equivalent of the regions in Figure 3 can be observed here in our data. Film growth, for each of the cases we present, was carried out over a wide range of parameter space. Tables I and II represent the data collected for this case. One of the advantages of pulsed metal deposition for probing phenomena related to wetting layers is that sub-monolayer deposition can be carried out, that is, partial metal adlayer coverage can be accomplished and monitored. Table I shows the results for sub-monolayer deposition per cycle (a monolayer of GaN being 0.259 nm in thickness). The RMS (root mean square) roughness values were obtained using AFM after etching with HCl:H 2O for 10 min to remove any surface oxide or residual gallium (the GaN layer is unaffected by this etch). The low roughness values shown in the table are consistent with the growth of Ga-face GaN films. An example AFM image is shown in Figure 4 with molecular terraces clearly visible in that example (though that example is actually from case (2), below). Ga-face GaN is usually grown at such low temperatures on GaN templates, or AlN buffer layers, here the MEAglow methodology has allowed the growth directly on sapphire. Hot KOH etching of some of the samples was carried out to check for Ga-face polarity and was confirmed by the lack of change in the sample surfaces.

Table II shows the surface roughness for thicker metal deposition per cycle. Some of these samples were so rough that film deposition per cycle could not be calculated. In fact, many of these samples showed evidence of nanopillar growth or of the onset of nanopillar growth (see Figure 5 for
an example). We have previously reported the deposition of InN nanopillars, but here we can reveal that the InN nanopillars grown with metal rich conditions required the presence of an RF induced positive potential above the sample. Growth of either InN or GaN nanopillars, under metal rich conditions, could not be initiated otherwise for the growth temperatures used.

For comparison to the surface structure results of Heying et al. shown in Figure 3, we calculated an equivalent to the Ga metal flux used in those MBE experiments. This was found by calculating to a first order estimate the total bombardment of the substrate surface with TMG molecules using standard kinetic gas equations and taking into account the TMG partial pressure. The bombardment data of both Tables I and II were used to compose the graph of Figure 6. The substrate temperatures were used for this calculation.

There are some differences when comparing Figure 6 with the graph of Heying et al.; here, the TMG has the added step of having to first decompose before supplying gallium atoms to the surface, and this occurs more effectively at the higher temperatures shown (above 575 °C). Also, the graph of Figure 6 is for pulsed metal deposition, not continuous growth, so the bombardment shown is for a single pulse of TMG. Because a pulsed metal deposition technique was used, the deposition is always in the gallium rich regime to begin with. The diagram also represents a wide assortment of data and has various nitrogen “flux” for the data points shown, so some of the rougher samples may be because of insufficient nitrogenation. It should be noted that, compared to MBE, for the higher pressures used for these experiments the temperature, pressure, and volume are all interactive through the ideal gas equation; it is therefore not possible to maintain the equivalent of a “constant” nitrogen flux when changing the growth temperature. Further, because there is a large pressure of un-activated nitrogen in the system, determination of a “flux” of active nitrogen species is not readily measured by direct means but is best determined indirectly by examination of the samples. This is a traditional method for CVD type experiments where greater complexity of parameter space may be present.

The simpler situation seen for MBE allows a very basic portrayal of data in the case of Heying et al. However, we can look for the equivalent situation here by examination of the samples grown. The absence of smooth samples (for the purpose of this paper, rather arbitrarily, smooth samples are defined in Figure 6 as having an RMS roughness of less than 0.1 nm), despite any variation of nitrogen delivery conditions (in particular, the time of nitridation), provides an indication of the boundary of the droplet regime. It can be seen that no smooth samples could be obtained for a Ga bombardment flux $>1 \times 10^{18}$ cm$^{-2}$. And for those samples that were smooth at lower Ga flux, almost all had sub-monolayer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth temperature (°C)</th>
<th>RMS roughness (nm)</th>
<th>nm/cycle</th>
<th>Film thickness (nm)</th>
<th>TMG bombardment (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>470</td>
<td>0.374</td>
<td>0.073</td>
<td>250</td>
<td>$3.12 \times 10^{17}$</td>
</tr>
<tr>
<td>2</td>
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</tr>
<tr>
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<td>0.10</td>
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</tr>
<tr>
<td>4</td>
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<td>1.66</td>
<td>0.146</td>
<td>500</td>
<td>$2.86 \times 10^{17}$</td>
</tr>
<tr>
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<td>0.19*</td>
<td>149*</td>
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</tr>
<tr>
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<td>$3.74 \times 10^{17}$</td>
</tr>
<tr>
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<td>0.107</td>
<td>110</td>
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</tr>
<tr>
<td>8</td>
<td>655</td>
<td>0.679</td>
<td>0.047</td>
<td>48</td>
<td>$2.86 \times 10^{17}$</td>
</tr>
<tr>
<td>9</td>
<td>660</td>
<td>1.13</td>
<td>0.067</td>
<td>69</td>
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<tr>
<td>10</td>
<td>660</td>
<td>1.73</td>
<td>0.078</td>
<td>80</td>
<td>$2.85 \times 10^{17}$</td>
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</tbody>
</table>

FIG. 4. Case (2) AFM image of GaN surface grown with zero potential at 630 °C, RMS surface roughness = 0.969 nm, molecular terracing clearly visible.
coverage per cycle. Nanopillars were formed in many instances of high TMG flux (as indicated in Table II). A small intermediate region could be identified in this graph, but with only one data point at low flux and high temperature.
that had RMS surface roughness of less than 2 nm for a deposition rate greater than a monolayer per cycle.

The boundaries for the three regions shown in Figure 6 are only approximations based partially on the positions of the smooth samples, and lack thereof. It is well known that the smoother GaN samples, associated with the deposition of a thicker (>1 monolayer) metal layer per cycle, are related to the presence of a wetting layer15 and may therefore belong to the intermediate region. The Arrhenius related shape of the boundary between the Ga droplet regime and the intermediate regime has been determined by Heying et al.15

Here, again, for this particular case, we have not determined its exact location though it is indicated approximately by the positions of the rougher samples.

The sub-monolayer region, which also has smooth samples, being for pulsed metal delivery data, has no exact equivalent in the surface diagram of Heying et al. but would be equivalent to the layer by layer growth regime more recently identified.16 For our case, the shape of the boundary for this layer has been roughly based on the TMG decomposition data of Bahlawane et al.,20 which has a marked increase at around 500–575 °C, but appears to be reasonably constant at lower temperatures. The higher decomposition of TMG above this temperature range would result in a greater quantity of gallium atoms on the sample surface, though again, the boundary shown is only an approximation.

The smooth surfaces of Table I were achieved over a temperature range of 470–660 °C; however, increasing the TMG delivery any further to increase the growth per cycle resulted in significant roughening of the GaN (despite any variation of nitrogen flux to compensate for the extra gallium). A wide range of growth parameters were attempted, however the results were inevitably the same, as shown in Table II. Growth per cycle could not be recorded for many of these films because of the severity of the surface roughness. In fact, as already mentioned, examination with SEM showed that for many samples there were nanostructures evolving on the surfaces from Ga droplets (see the example in Figure 5). A similar effect was observed for InN deposition. Free Ga metal could not be observed in X-ray diffraction for the GaN samples, as gallium is a liquid near room temperature and is amorphous. For InN, however, XRD showed significant amounts of free indium in these films. We have reported on the morphology of these InN nanopillars previously,17–19 but without elucidation of the growth mechanism, which we provide here in Sec. IV.

The inability to deposit more than sub-monolayer cycles for smooth layers grown at lower temperatures (below the intermediate region) indicates that wetting layers were not being achieved under those deposition conditions but that metal droplets were instead forming when the sub-monolayer coverage grew to a certain point. This issue is addressed further in Section IV.

Table III indicates a number of samples grown with ≥1 monolayer of GaN/cycle. Very smooth samples were achieved for above monolayer deposition per cycle over a much larger temperature range than for case (1), though the optical transmission measurements for many of these samples showed evidence of below band-gap absorption that is typical of the presence of excess gallium in the film (see, for example, the gallium rich growth examples in Figure 3 of MacKenzie et al.21). An example is shown in Figure 7. The band-gap, found from the standard technique of extrapolating an absorption coefficient squared plot to the x axis in its linear region,22 appeared to be 3.25 eV. This is below the ~3.4 eV expected for pure GaN and is typical of metal rich films.21 We observed a further shift to even lower values for more gallium rich growth conditions than those of the example shown. Others have reported the inclusion of gallium metal during the low temperature growth of GaN.23 In particular, at temperatures below about 600 °C, the thermal desorption of excess gallium is negligible, so that the incorporation of unreacted gallium atoms (in our case, possibly with methyl ligands, given the use of metalorganics) might

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth temperature (°C)</th>
<th>RMS roughness (nm)</th>
<th>nm/cycle</th>
<th>Film thickness (nm)</th>
<th>TMG bombardment (cm²⁻)</th>
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<tr>
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<tr>
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<td>0.969</td>
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<td>50</td>
<td>2.89 x 10¹⁸</td>
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</table>

Table III. Case (2) film growth results for samples with less than 2 nm RMS surface roughness. Those samples with an asterisk had their film thickness measured by optical transmission spectroscopy, while the others were measured by SEM profile images.
be expected. However, we see no distinct chemical differences in the films for the cases of positive or no applied potential above the sample.

Nanopillars could not be grown under these conditions. These are the conditions under which VLS (vapour-liquid-solid) nanopillar growth might be expected to occur. Instead, as we had previously reported, when metal droplets were formed on the sample surface they were partially nitrided on their tops and sides. Without the presence of an electric field, and at these temperatures, there does not seem to have been an effective driving force to allow deposition on the substrate from the melt of a metal droplet. Other groups have observed similar results in the same temperature range as described in greater detail in the discussion below.

In a similar fashion to Figure 6, Figure 8 shows a surface structure diagram for case (2), based on the data of Tables III and IV. The data in Table IV provide above monolayer deposition for some examples of rougher films where nitridation conditions were not always optimised for the cycles of growth, though film thicknesses were not determined in all those cases. For Figure 8, it is immediately apparent that the region where smooth samples can be grown has expanded considerably. The intermediate region based on smooth samples with 1 monolayer/cycle or more has shifted to lower temperature and higher TMG bombardment flux. The boundaries shown are again approximate, based on the location of the data, with the exception of the data at 616°C, where the boundary between the intermediate and droplet regimes was established for those conditions and where considerable effort was made to determine optimum nitridation conditions.

It is to be noted that under extreme plasma conditions (low pressure, high gas flow from the plasma source), the plasma could be extended beyond grid A so that the substrate once again saw a positive potential. Under these conditions, nanopillars could again be grown under metal rich conditions, though in this case the TMG bombardment was above the scale of Figure 8.

D. Case (3) grid C in place

Examination of the changes made between cases (1) and (2) above suggested to us that the electric field was important for the control of metal wetting layers. The floating DC potential of +78 V at 4 cm above the sample holder, for a remote plasma configuration, suggested a driving force for nanopillar growth for case (1) (see discussion, below). However, the presence of grid A resulted in the loss of a large proportion of active nitrogen species, severely limiting the growth rate. The hole configuration of grid A restricted the exit area of the plasma to 57% of what it would be in its absence. Loss of active species through wall recombination would be severe in that case.

We therefore removed grids A and B and put grid C in place with the ability to bias that grid. This grid was closer to the sample and had a more open configuration, which,

![FIG. 7. Absorption coefficient squared versus energy plot from UV-Vis data transmission data for 68 nm sample grown with TMG bombardment of 2.85 \times 10^{18} \text{ cm}^{-2}.

![FIG. 8. Surface structure diagram for case (2), from data of Tables III and IV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth temperature (°C)</th>
<th>RMS roughness (nm)</th>
<th>Nm/cycle</th>
<th>Film thickness (nm)</th>
<th>TMG bombardment (cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>482</td>
<td>2.42</td>
<td>0.74</td>
<td>148*</td>
<td>8.97 \times 10^{17}</td>
</tr>
<tr>
<td>61</td>
<td>484</td>
<td>6.96</td>
<td>0.71</td>
<td>142*</td>
<td>1.26 \times 10^{18}</td>
</tr>
<tr>
<td>62</td>
<td>506</td>
<td>9.5</td>
<td>0.8</td>
<td>160*</td>
<td>8.91 \times 10^{17}</td>
</tr>
<tr>
<td>63</td>
<td>616</td>
<td>6.54</td>
<td>...</td>
<td>...</td>
<td>3.88 \times 10^{18}</td>
</tr>
<tr>
<td>64</td>
<td>616</td>
<td>14.0</td>
<td>...</td>
<td>...</td>
<td>2.96 \times 10^{18}</td>
</tr>
<tr>
<td>65</td>
<td>616</td>
<td>10.5</td>
<td>...</td>
<td>...</td>
<td>2.96 \times 10^{18}</td>
</tr>
<tr>
<td>66</td>
<td>616</td>
<td>2.28</td>
<td>0.458</td>
<td>330*</td>
<td>2.96 \times 10^{18}</td>
</tr>
</tbody>
</table>
unlike grid A, allowed the passage of a large proportion of active neutral species. An increase in growth rate was noted (approximately double) for many conditions compared to case (1).

Using this configuration, we could recreate the bias conditions of case (1), above, by floating grid C, or by applying a positive bias to the grid. In these circumstances, nanopillars could be grown again, as per case (1). An example of this is shown in Figure 9, for which surface SEM images are provided for two InN samples. The two samples were grown under exactly the same conditions; however, Grid C was biased to +43 V for the sample with nanopillars, the sample without had grid C grounded. The sample without nanopillars was rough with a polycrystalline habit. There is a shift in parameter space between the two situations, which requires some optimisation. Optimised, better quality InN layers are reported elsewhere.31

For GaN, we could replicate the zero bias conditions of case (2) by grounding grid C. This allowed us to grow smooth (as defined above, with RMS surface roughness <2 nm) GaN samples, again, over a wide temperature range. An example is shown in Figure 10. That sample was grown at 0.248 nm/cycle or at about 1 monolayer per cycle to a thickness of 210 nm. The AFM image provides an RMS roughness of 0.68 nm. For this sample and others, we concentrated our efforts on growing above the dissociation temperature of the TMG (indicated in Figures 6 and 8) at >580°C using as a starting point a standard growth recipe developed for case (1) using sub-monolayer deposition at temperatures that appeared to be just below the intermediate region of Figure 6. As we mention above for InN, for GaN there is a shift in parameter space when applying bias to grid C that is more negative than the DC potential of the plasma. Much more gallium is evident in the films with increasingly negative applied grid voltage. These results are still being interpreted and will be presented in more detail at a later date, but it is clear at this point that a graph comparative to Figures 6 and 8 needs further interpretation for case (3).

That being said, we had been unsuccessful in increasing the growth per cycle of this recipe previously under case (1), but under negative and grounded grid C conditions we were able to increase the growth per cycle while maintaining sample smoothness (as per case (2)).

IV. DISCUSSION

The basic problem being contended with in this paper was the results of case (1). For those results, it was found that there was an inability to grow smooth layers (<2 nm RMS roughness) when depositing more than a sub-monolayer of material per cycle outside of a small intermediate zone. Examination of the literature shows mixed and inconsistent results from deposition experiments with pulsed metal delivery. For the pulsed metal deposition results of the Japanese group from Sophia University,32,33 they were only able to achieve smooth surfaces when depositing up to 0.2 nm/cycle (i.e., equivalent to less than a monolayer), at higher deposition per cycle gallium droplets and increased surface roughness resulted.

In contrast, a Georgia Institute of Technology group, Burnham et al.,11 reported deposition of up to 3.9 nm/cycle
at 550°C using their metal modulated technique and were able to deposit smooth layers despite some gallium droplet formation (and subsequent nitridation) during each cycle. Goff et al. have reported deposition of up to approximately 2 monolayers of gallium per cycle for their deposition using anion modulation down to 500°C. Although details of that report are sparcely provided, they avoided Ga droplet formation (presumably due to an accompanying increase in surface roughness).

Another Georgia Institute of Technology group, Tong et al., has provided an earlier report using a more traditional migration enhanced epitaxy with deposition of up to 6 nm/cycle to achieve very smooth surfaces on silicon substrates. Their results rival those of Burnham et al., and again there appear to have been no detrimental effects from gallium droplet formation.

Clearly, these reports show variation in the effect of the presence of gallium droplets, but also on the limits of thickness of GaN that could be deposited per cycle without increasing sample surface roughness substantially. The gallium wetting layer (adatom layer) present during growth appears to be critical for some of these reports and for our own results here. In our case, that of the Japanese Sophia University group and that of Goff et al., the results for smooth layers were limited to below the threshold of gallium droplet formation. Similar results have been achieved for traditional MBE growth, where the gallium droplet regime is avoided when smooth film deposition is required (the intermediate regime being preferred).

In contrast, Burnham et al. were able to still achieve smooth layers with some Ga droplet formation (though apparently these were fully nitrided into smooth layers during each cycle without further droplet accumulation). While the earlier report of Tong et al. does not address the issue of Ga droplets, it does not appear to have been problematic for them for quite large deposition per cycle on silicon, though in that case the conducting nature of the silicon may have been influential.

Here, we concentrate on the issue of the different maximum deposition per cycle that were achieved before gallium droplet formation, though we believe the ability to, in some cases, nitride gallium droplets into smooth layers may be related to some of the effects we identify. The boundary of formation for gallium droplets is strongly related to the formation of the gallium wetting layer (adatom layer) on the surface of samples. Recently, Rossow et al. have also identified the importance of the metal wetting layer and have pointed out that there is some variation in published results for the maximum thickness of metal wetting layers used for nitride deposition. Butcher identified this importance earlier in patent applications. While Misra et al. have reported variations in the thickness of gallium wetting layers for different substrate planes, dependent on whether a plasma was present or not.

The work of Northrup et al. is most commonly referenced in relation to the existence of the gallium wetting layer and provides calculations and experimental evidence for the existence of a liquid metal gallium bilayer being present on the surface of GaN in the gallium rich limit before the formation of Ga droplets. The bilayer was calculated to contain 2.33 monolayers of gallium by Northrup et al. and its presence should apparently be temperature dependent. The intermediate zone, identified by the work of Heying et al. and by the earlier work of Hacke et al. exists because the parameter space over which the wetting layer exists is broadened by thermal evaporation from the GaN surface as temperatures increase. However, the gallium wetting bilayer, as a boundary to gallium droplet formation, has been assumed to exist over a wide range of temperatures, even below the intermediate regime, though it would be difficult to confirm this situation by conventional MBE deposition. As previously mentioned, pulsed metal deposition has been used here to probe wetting layer thickness.

The case (1) results, and those of the Sophia University group indicate that, for these situations, a full monolayer coverage of gallium could not be achieved before gallium droplet formation occurred. So essentially, the gallium bilayer was missing in these instances. This is an extraordinary result, apparently in conflict with theoretical prediction. This required further investigation on our part. The case (2) results were fundamental to understanding the basic physics underlying these case (1) observations. The absence of nanopillar formation in case (2) was particularly elucidating.

The growth of nanopillars in the droplet regime for case (1) above and the lack of growth of nanopillars for case (2) (and for case (3) when the grid was grounded or negatively biased) are problematic. For case (1), the nanopillars were growing upwards against gravity from droplets of metal (indium or gallium) toward the positive potential measured above the substrate and created by the RF plasma source. The metal was accumulating as droplets on the nanopillar heads with the deposited metal apparently migrating to the top of the nanopillars rather than depositing on other parts of the substrate or on the side walls of the nanopillars. This is evidenced by the SEM images of Figures 5 and 9, showing droplets with the nanopillars growing at the base of the metal droplet and with the gallium nitride or indium nitride pillar diameter being determined by the droplet width. Often the growth rates of the nanopillars were quite high compared to that of continuous layer growth, for gallium nitride nanopillars, the growth rates could be in excess of 1 μm/h, which was approximately an order of magnitude higher than for any of the continuous GaN films grown here.

Additionally, it is to be noted that these nanopillars were circular in cross-section and grown under metal rich conditions, not under the nitrogen rich growth conditions for which nanopillars of hexagonal cross-section are commonly observed. The formation of hexagonal nanopillars under nitrogen rich conditions requires more aggressive plasma conditions than the remote plasma conditions used here. As noted for the above results of case (2), nanopillars failed to grow under those zero bias, metal rich conditions, even by a VLS path. Instead any gallium (indium) droplets that formed were just nitrided on their outer surfaces; similar results have been noted by others. It appears that the lack of VLS growth was because of insufficient liquid metal convection currents within the droplets at these low deposition temperatures. The mechanisms for transporting nitrogen saturated metal to the underside of the droplets were
therefore absent. Higher temperatures and/or longer nitridation periods would be required for VLS deposition.

The lack of a VLS mechanism for case (2) suggests that for case (1) the nanopillars were growing by a different mechanism entirely. We identify that mechanism to be an electric field assisted VLS, or, more properly an electro-epitaxy type of LPE. LPE mechanisms have been proposed before in the case of MBE and CVD type growth involving pulse deposition of metal layers. However, a temperature differential is required for thermal LPE to occur and in this case the temperature differential is in the wrong direction. For LPE, the substrate must be cooler than the melt, while here the substrate is heated from below and a rapid temperature drop off has been measured away from the substrate. As pointed out by Novikov and Foxon for their MBE growth, there appears to be no thermal driving force for the LPE of group III metals for nitride based thin film growth using plasmas.

LPE requires a temperature differential (in the right direction) or an electrical differential across a melt to drive epitaxy. Novikov and Foxon used electro-epitaxy to achieve LPE of gallium nitride in an MBE system with a nitrogen plasma, in that case applying an electric field differential directly to a metal melt. It was recognised that in our case there is also an electrical differential or potential. The driving force for nanopillar formation in case (1) is the DC electrical potential provided by the RF plasma.

As mentioned previously in Section II, a RF plasma operating at 13.56 MHz develops a positive DC potential. It is known from the development of ion source technology for accelerators that a positive potential will attract metals in a vacuum. There are publications showing the attraction and movement of liquid gallium metal toward a positive potential. Other liquid metals, or even solid metals, can behave similarly; in fact, this is part of the basis of the field of electrohydrodynamics. Therefore, for LPE based electro-epitaxy to occur, there is in fact no need to contact the liquid melt with physical electrodes, as was done by Novikov and Foxon. An electrostatic field can produce the required field differential across the liquid melt. In case (1), an electrostatic potential was present, measured to be +78 V at 4 cm above the substrate holder. This appears to have been an adequate driver for the LPE electro-epitaxy of the nanopillars for that particular case. Also in case (3), the result was replicated by applying positive volts to grid C (see Figure 9) or by floating that grid.

The positive electrostatic potential present in case (1) also explains the inability to produce smooth GaN films when depositing a monolayer or more of material for pulse metal deposition. Sub-monolayer deposition per cycle could deposit smooth GaN layers; however, when the gallium metal coverage became too great, the positive electrostatic potential “pulled” the negatively charged gallium into droplets. In that case, a complete wetting layer coverage of the sample surface could not be achieved. In contrast, very smooth GaN could be deposited with higher metal coverage when there was no electrostatic potential present. In case (2), more than 1 monolayer per cycle could be deposited at exceptionally low temperatures so that a metal wetting layer was present at those temperatures.

These results indicate that the boundary between the “droplet regime” and “intermediate regime” in Figures 6 and 8 is not just dependent on temperature, as indicated by the Arrhenius characteristic determined by Heying et al. but is also strongly dependent on the electrostatic field, which is temperature independent. Part of the wide variation of reported values for maximum wetting layer thickness may be explained by electrostatic variations in the various growth systems used. The change in wetting layer thickness observed by Misra et al. when the plasma source was on may similarly be explained as the result of a change in the applied electrostatic field.

It is worth noting that plasma sources are only one source of electrostatic fields in MBE systems; ion gauges, RHEED guns, and other diagnostic devices can also contribute to the electrostatic potentials “seen” by a sample. The particular orientation of electrostatic fields may also be significant and may help explain the ability to nitride small metal droplets into smooth films in some systems, whereas for others, the field alignments would eliminate that possibility entirely.

Finally, it is worth examining the effect that such electrostatics (between the plasma and sample) can have on film growth rate. For our case (1), grid A was purposely absent to try and increase the growth rate. As mentioned in case (3) Section III, grid A severely limited the flux from the plasma source. Additionally, because the active nitrogen flux from our source was not part of a low pressure “beam” (as in MBE) but flowed from the source, for our system the plasma flux was dispersed over such a large area (a 10.75 in. internal chamber diameter, sized for future expansion) that there was a significant loss of growth rate as a result. The ~4 in. (10 cm) diameter growth area would only have seen about 14% of the total nitrogen flux if that were evenly distributed over the whole chamber area. A smaller chamber and higher power plasma source were preferable for increased growth rate in this case, but only obtainable with considerable equipment modification.

To obtain reasonable growth rates, it was therefore preferable to not have grid A in place. Removing this grid may have increased the nitrogen flux by as much as a factor of 1.75, when comparing case (1) with case (2). However, the positive electrostatic potentials present in case (1) were so strong that they compromised the continuity of the metal wetting layer, so that the bilayer expected from theory was absent. Therefore, instead of the approximate 1.75 fold increase in growth rate expected with the removal of grid A, and the resulting nitrogen flux increase, there was a substantial decrease in the maximum growth rate that could be achieved before gallium droplet formation occurred.

Figure 11 shows, for smooth samples (for the examples of Figure 11 we define “smooth” as <1 nm RMS surface roughness, though elsewhere we use <2 nm growth rate versus TMG bombardment per pulse for case (1) and case (2) data. The case (2) samples shown in the figure were all grown under the same conditions, and only the TMG flow rate was changed (to vary the TMG bombardment per pulse). Also shown on the graph is the maximum growth rate sample in case (1) for approximately the same growth temperature. Obviously, the increase in nitrogen flux for the case (1)
samples did not help improve their growth rates. By compromising the presence of the gallium wetting layer, the positive potential of the plasma source acted to limit the growth rates for that case to less than half those achieved for case (2).

Though we have presented mainly pulsed metal deposition data, the observations made also have implications for conventional film growth with plasma sources. For instance, our results may explain an apparent inconsistency observed by Kawai et al. who, for a 1000 fold increase in active nitrogen species from a new MBE plasma source, were only able to achieve a factor of 3 increase in GaN growth rate. Beyond that increase they also observed gallium droplet formation. That lower than expected increase in GaN growth rate may have resulted, in part, because of a higher positive potential from the new plasma source, which caused the metal wetting layer to be electrostatically compromised. This effect would mimic what is usually believed to be a nitrogen flux limit as evidenced by the formation of gallium droplets.

This mimicking of nitrogen limited growth may have quite broad consequences. Many MBE systems, and other types of plasma growth system, may actually be compromising maximum attainable growth rates through uncontrolled electrostatic interactions with metal wetting layers. It should also be noted that although we have concentrated on looking at nitride based films, the described electrostatic interactions with wetting layers are quite general and may have implications for other material systems.

V. CONCLUSIONS

In this paper, we have shown that attractive electrostatic interactions between positive DC charge regions in RF plasmas and negatively charged metal wetting layers can have a very strong influence on compound semiconductor thin film growth morphology. In particular, these electrostatic interactions can affect metal rich growth limits by the formation of metal droplets under the positive potential presented by RF plasma sources. In turn, this can limit the growth rate. By shielding the positive DC potential of the plasma, we were able to more than double the growth rate observed here.

It has also been shown that electrostatic attraction can enhance spontaneous nanopillar growth through an electropitaxy growth mechanism. For the examples of InN and GaN presented here, it is shown that the VLS nanopillar growth mechanism was absent for the low growth temperatures used and that the presence of the positive electrostatic potential of the RF plasma was necessary for the nanopillar growth to proceed. Alternately, in the absence of positive electrostatic potentials, nanopillar growth could be suppressed in favour of very smooth layers with RMS surface roughness below 2 nm in the presence of metal wetting layers, even for GaN growth temperatures as low as 490 °C.

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