ABSTRACT
GaN films have been grown on 6H-SiC substrates employing a new form of selective lateral epitaxy, namely pendeo-epitaxy. This technique forces regrowth to start exclusively on sidewalls of GaN seed structures. Both discrete pendeo-epitaxial microstructures and coalesced single crystal layers of GaN have been achieved. SEM and TEM analysis are used to evaluate the morphology of the resulting GaN films. Process routes leading to GaN pendeo-epitaxial growth using silicon substrates have also been achieved and the preliminary results are discussed.

INTRODUCTION
The III-nitride scientific community has been forced to grow thin films of GaN and related nitride materials using heteroepitaxial growth routes and techniques because of the dearth of bulk substrates of these materials. The resultant $10^8 - 10^{10}$ cm$^{-2}$ density of threading dislocations limits the properties of the resulting films and the devices fabricated in these materials. As such, there has been substantial research regarding selective area growth (SAG) and lateral epitaxial overgrowth (LEO) techniques for GaN deposition [1-9], fueled in part by the recent announcement by Nakamura, et al. [10] of the dramatic increase in projected lifetime of their GaN-based blue light-emitting laser diodes fabricated on LEO material. Using these approaches, researchers have been able to grow GaN films containing dislocation densities of $\approx 10^5$ cm$^{-2}$ in the areas of overgrowth. However, to benefit from this reduction in defects, the placement of devices incorporating LEO technology is limited and confined to regions on the final GaN device layer that are located on the overgrown regions.

In this paper, we report the achievement of a new approach to selective epitaxy of GaN, namely, pendeo- (from the Latin: to hang or be suspended) epitaxy (PE) as a promising new process route leading to a continuous, large area layer or discrete platforms of this material. An initial form of GaN pendeo-epitaxy without the use of a seed-mask was first reported by Zheleva et.al. [11]. The current approach incorporates mechanisms of growth exploited by the conventional LEO process by using an amorphous mask to prevent vertical propagation of threading dislocations; however, it extends beyond the conventional LEO approach to employ the substrate itself as a pseudo-mask as discussed by Linthicum et.al. [12]. This unconventional approach differs from LEO in that growth does not initiate through open windows on the (0001) surface of the GaN seed layer, instead it is forced to selectively begin on the side walls of a
tailored microstructure comprised of forms previously etched into the seed layer. Continuation of
the pendeo-epitaxial growth until coalescence over and between these forms results in a complete
layer of low defect-density GaN. This is accomplished in one regrowth step, and the need to
align devices or masks for the growth of a second layer over particular areas of overgrowth on the
final GaN layer is eliminated. This approach may be more widely applicable than just GaN, as
indicated by Gehrke et.al. [15]. Additionally, we report for the first time the ability to grow
GaN pendeo-epitaxial films on silicon substrates. The achievement of GaN layers with surface
areas limited only by the size of the available silicon substrates is now conceivable.

The following sections describe the experimental parameters necessary to achieve GaN
films via PE, describe and discuss the microstructural evidence obtained for the resulting films
and provide a summary of this research.

EXPERIMENTAL PROCEDURES

Each pendeo-epitaxial GaN film and the underlying GaN seed layer and the AlN buffer
layer were grown in a cold-wall, vertical pancake style RF inductively heated metalorganic vapor
phase epitaxy (MOVPE ) system. Two distinct process routes were explored for growth on (i)
on-axis (0001)6H-SiC substrates and (ii) on-axis (111)Si substrates. In the former, each seed
layer consisted of a 1 µm thick GaN film grown on a 100 nm thick AlN buffer layer previously
deposited on a (0001) 6H-SiC substrate. Details of the experimental parameters used for the
growth of these two layers are given in Ref. 13. In the growth on the Si substrates, a 1 µm
(111)3C-SiC film was initially grown on a very thin (111)3C-SiC layer produced by conversion
of the (111)Si surface via reaction with C\textsubscript{3}H\textsubscript{8} entrained in H\textsubscript{2}. Both the conversion step and SiC
film deposition were achieved using a cold-wall, vertical geometry, RF inductively heated
atmospheric pressure chemical vapor deposition (APCVD) reactor. Details of the experimental
parameters used for the conversion step and the growth of the 3C-SiC layer are given in Ref. 14.
A 100 nm thick AlN buffer layer and a 1 µm GaN seed layer were subsequently deposited in the
manner used for the 6H-SiC substrates and noted above.

A 100 nm silicon nitride growth mask was deposited on the seed layers via plasma
enhanced CVD. A 150 nm nickel etch mask was subsequently deposited using e-beam
evaporation. Patterning of the nickel mask layer was achieved using standard photolithography
techniques followed by dipping in HNO\textsubscript{3} for approximately five minutes. The samples were
subsequently cleaned by consecutive dips in trichloroethylene, acetone, methanol, and HCl for
five minutes each and blown dry with nitrogen. The final, tailored, microstructure consisting of
seed forms was fabricated via removal of portions of the nickel etch mask via sputtering and by
inductively coupled plasma (ICP) etching of portions of the silicon nitride growth mask, the GaN
seed layer and the AlN buffer layer. Critical to the success of the pendeo-epitaxial growth, the
etching of the seed-forms was continued completely through the exposed GaN and AlN layers
and into either the 6H-SiC substrate or the 3C-SiC layer, thereby removing all III- nitride material
from the areas between the side walls of the forms. The seed-forms used in this study were
raised rectangular stripes oriented along the <1-100> direction, thereby providing a plurality of
GaN sidewalls (nominally (11-20) faces). Seed form widths of 2 and 3 µms coupled with
separation distances of 3 and 7 µms, respectively, were employed. The remaining nickel mask
protecting the seed structures during the ICP etching process was removed using HNO\textsubscript{3}.
Immediately prior to pendeo-epitaxial growth, the patterned samples were dipped in a 50% HCl
solution to remove the surface oxide from the walls of the underlying GaN seed structures.
A schematic of the pendeo-epitaxial growth of GaN is illustrated in Figure 1. There are three primary stages associated with the pendeo-epitaxial formation of this material: (i) initiation of lateral homoepitaxy from the sidewalls of the GaN seed, (ii) vertical growth and (iii) lateral growth over the silicon nitride mask covering the seed structure. Pendode-epitaxial growth of GaN was achieved within the temperature range of 1050-1100°C and a total pressure of 45 Torr. The precursors (flow rates) of triethylgallium (26.1 µmol/min) and NH₃ (1500 sccm) were used in combination with a H₂ diluent (3000 sccm). Additional experimental details regarding the pendeo-epitaxial growth of GaN and AlₓGa₁₋ₓN layers employing 6H-SiC substrates are given in Refs. 15, 16, and 17. The morphology and defect microstructures were investigated using scanning electron microscopy (SEM) (JEOL 6400 FE) and transmission electron microscopy (TEM) (TOPCON 0002B, 200 KV).

RESULTS AND DISCUSSION
The pendeo-epitaxial phenomenon is made possible by taking advantage of growth mechanisms identified by Zheleva et al.[7] in the conventional LEO technique, and by using two additional key steps, namely, the initiation of growth from a GaN face other than the (0001) and the use of the substrate (in this case SiC) as a mask. By capping the seed-forms with a growth mask, the GaN was forced to grow initially and selectively only on the GaN sidewalls. Common to conventional LEO, no growth occurred on the silicon nitride mask covering the seed forms. Deposition also did not occur on the exposed SiC surface areas at the higher growth temperatures employed to enhance lateral growth. The Ga- and N-containing species more likely either diffused along the surface or evaporated (rather than having sufficient time to form GaN nuclei) from both the silicon nitride mask and the silicon carbide substrate. The pronounced effect of this is shown in Figure 2 wherein the newly deposited GaN has grown truly suspended (pendeo-) from the sidewalls of the GaN seed structure. During the second PE event (ii), vertical growth of GaN occurred from the advancing (0001) face of the laterally growing GaN. Once the vertical growth became extended to a height greater than the silicon nitride mask, the third PE event (iii) occurred, namely, conventional LEO-type growth and eventual coalescence over the seed structure, as shown in Fig. 3. A cross-sectional TEM micrograph showing a typical pendeo-epitaxial growth structure is shown in Fig. 4. Threading dislocations extending into the GaN seed structure, originating from the GaN/AlN and AlN/SiC interfaces, are clearly visible.
The silicon nitride mask acted as a barrier to the further vertical propagation of these defects into the laterally overgrown pendeo-epitaxial film. Since the newly deposited GaN is suspended above the SiC substrate, there are no defects associated with the mismatches in lattice parameters between GaN and AlN and between AlN and SiC. Preliminary analysis of the GaN seed/GaN pendeo-epitaxy interface revealed evidence of threading dislocations or stacking faults within the (0001) planes. This indicates evidence of the lateral propagation of the defects, however, there is yet no evidence that the defects reach the (0001) surface where device layers will be grown. As in the case LEO, there is a significant reduction in the defect density in the regrown areas.

The continuation of the pendeo-epitaxial growth results in coalescence with adjacent growth fronts and the formation of a continuous layer of GaN, as observed in Figure 5. This also results
in the practical elimination of all dislocations stemming from the heteroepitaxial growth of GaN/AlN on SiC. Clearly visible in Fig. 5(a) are the voids that form when adjacent growth fronts coalesce. Optimization of the pendeo-epitaxial growth technique should eliminate these undesirable defects.

The maximum diameter of commercially available 6H- and 4H-SiC substrates is currently limited to approximately two inches. As such, the development of a process route for achieving the pendeo-epitaxial growth of (0001)GaN on (111)Si was undertaken. Unlike silicon carbide and sapphire substrates, the development of process routes leading to the growth of GaN films on silicon substrates have lagged behind. The slow progress has been due in part to the difficulty in the nucleation and two dimensional growth of GaN caused by a combination of significant mismatches in lattice parameters and coefficients of thermal expansion and the chemical stability of the phases in the growth environment. To address these concerns, a 3C-SiC transition layer was employed between the Si wafer and the AlN buffer layer for three reasons. Firstly, an on-axis (111)Si substrate was used which allowed for deposition of the (111)3C-SiC polytype. The SiC layer is preferred for the growth of the 2H-AlN buffer layer of sufficient quality for the subsequent growth of the single crystal GaN seed layer. Secondly, as described above, PE growth of GaN is obtained on SiC because under the growth conditions used for this growth, Ga and N atoms will not bond to the SiC surface in numbers and in time sufficient to cause gallium nitride nuclei to form. Thirdly, the 3C-SiC layer is needed as a diffusion barrier to prevent the interaction of Si atoms with the Ga and N species found in the growth environment. If there is either no diffusion barrier or a diffusion barrier of insufficient thickness, the Si atoms from the substrate have sufficient energy at the temperatures used for PE growth to diffuse to the surface of the AlN buffer layer and react with the gallium nitride layer. This results in the formation of large voids in the underlying Si substrate, the “poisoning” of the GaN film, and the formation of polycrystalline GaN-containing material.

![Figure 6. Cross-sectional SEM of pendeo-epitaxial GaN grown on a (111)Si substrate. Clearly visible is the rough surface morphology of the AlN buffer layer and 3C-SiC transition layer.

Figure 7. Low magnification cross-sectional SEM of pendeo-epitaxial GaN on a (111)Si substrate and a 3C-SiC transition layer showing coalescence over and between GaN seed forms.

The results of an SEM analysis of PE-grown GaN on a (111)Si substrate is shown in Fig. 6. The rough surface morphologies of the (111)3C-SiC and the AlN buffer layer as well as the
relatively poor quality of the GaN seed layer are clearly visible. In contrast, the pendepo-epitaxially grown GaN is of relatively superior quality in terms of surface roughness. Analysis via TEM of the PE GaN layer and optimization of the process routes to improve the PE technique using 3C-SiC are the subjects of ongoing research. Finally, Figure 7 shows a SEM image of coalesced pendepo-epitaxially grown GaN on a silicon substrate.

CONCLUSION

We have reported on the development of pendepo-epitaxial process routes as a potential way of growing uniformly low-defect density thin films over the entire surface of a substrate. In particular, we have achieved a method to grow GaN using pendepo-epitaxy on 6H-SiC substrates. We have demonstrated both discrete pendepo-epitaxial structures and coalesced layers of GaN. In addition, we report our preliminary results regarding the ability to grow pendepo-epitaxial GaN on silicon substrates. This latest development provides a possible pathway for the fabrication of device quality GaN thin films grown on large area silicon wafers.

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