Pendeoepitaxy of gallium nitride thin films

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Pendeoepitaxy, a form of selective lateral growth of GaN thin films has been developed using GaN/AlN/6H-SiC(0001) substrates and produced by organometallic vapor phase epitaxy. Selective lateral growth is forced to initiate from the $(11\bar{2}0)$ GaN sidewalls of etched GaN seed forms by incorporating a silicon nitride seed mask and employing the SiC substrate as a *pseudomask*. Coalescence over and between the seed forms was achieved. Transmission electron microscopy revealed that all vertically threading defects stemming from the GaN/AlN and AlN/SiC interfaces are contained within the seed forms and a substantial reduction in the dislocation density of the laterally grown GaN. Atomic force microscopy analysis of the $(11\bar{2}0)$ face of discrete pendeoepitaxial structures revealed a root mean square roughness of 0.98 Å. The pendeoepitaxial layer photoluminescence band edge emission peak was observed to be 3.454 eV and is blueshifted by 12 meV as compared to the GaN seed layer. © 1999 American Institute of Physics. [S0003-6951(99)03128-9]

The III-nitride materials have been recognized for several decades for their potential and, recently, for their commercial viability in wide band gap optoelectronic device applications including green and blue light emitting diodes and laser diodes.¹⁻³ Ultraviolet light detectors and high-temperature, high-power, and high-frequency microelectronic devices with promising characteristics have also been fabricated in the laboratory. Hindered by the lack of an ideal substrate, it has been necessary to grow essentially all III-N films using heteroepitaxial routes. As such, most films contain dislocation densities of 10^8 – 10^{10} cm⁻². As these defects very likely compromise the optimum attainable electrical and optical properties, it is of considerable importance to attain III-N materials and device structures with markedly decreased dislocation densities.

Recently, there has been a significant increase in activity in the use of selective area growth (SAG) in tandem with lateral epitaxial overgrowth (LEO)⁴⁻¹² to produce GaN films containing defect densities of $\approx 10^4$ cm⁻² in selected areas. This renewed activity was fueled in part by the recent announcement by Nakamura *et al.*¹³ of the significant projected increase in the lifetime of their blue laser diode by employing the LEO technique for the growth of the underlying GaN layer.

We report on a form of selective epitaxy of thin films, hereby referred to as *pendeoepitaxy* (PE), for achieving a more uniformly low density of defects in the material. Pendeoepitaxy (from the Latin: *pendeo*—to hang, or to be suspended) incorporates mechanisms of growth exploited by the conventional LEO process by using masks to prevent vertical propagation of threading defects, and extends the phenomenon to employ the substrate itself as a *pseudomask*. This approach differs from conventional LEO in that growth

does not initiate through open windows but begins on sidewalls etched into the GaN seed layer, as shown schematically in Fig. 1 and pictorially in the scanning electron micrograph in Fig. 2. As the lateral growth from the sidewalls continues, vertical GaN growth begins from the newly forming (0001) face of the continually extending lateral growth front. Subsequently, once the vertical growth reaches the top of the seed mask, lateral growth over the masked top of the seed begins, utilizing the conventional LEO technique. Allowing pendeoepitaxial growth to continue will result in coalescence over and between each seed form, producing a continuous layer of GaN. This is accomplished in one regrowth step and eliminates the need to align devices or masks for a second LEO layer over particular areas of the GaN surface. This is an alternative approach to our initial reported study,¹⁴ where no silicon nitride mask was employed and GaN growth initiated on both the top and the sidewalls of the GaN seed structures. This allowed for the vertical propagation of threading defects from the seed structures into the newly deposited growth, similar to conventional LEO growth.

The PE GaN and the underlying nitride seed layers were grown in a coldwall, vertical pancake style, rf inductively

FIG. 1. Schematic diagram showing pendeoepitaxial growth of GaN from etched GaN seedform $(11\bar{2}0)$ sidewalls.

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FIG. 2. Cross-sectional scanning electron micrograph of the initial stage of GaN pendeoepitaxy grown on a $2\text{ }\mu\text{m}$ wide GaN seed stripe oriented along the $\langle 1\bar{1}00 \rangle$ direction.

heated metalorganic vapor phase epitaxy system. The seed layers on which the PE GaN was grown consisted of a 100 nm thick AlN buffer layer and a $1\text{ }\mu\text{m}$ thick GaN layer grown on a 6H-SiC(0001) substrate. Details of the experimental parameters used for the growth of the nitride seed layers are given in Ref. 15.

A 100 nm silicon nitride mask was deposited on the GaN seed layer via plasma enhanced chemical vapor deposition. A 150 nm nickel etch mask was subsequently deposited using *e*-beam evaporation and patterned via standard photolithography techniques. The nitride seed microstructures were formed by removal of exposed nickel stripes via sputtering and by inductively coupled plasma (ICP) etching of the silicon nitride and GaN seed layers. Etching of the seed microstructure was continued completely through the nitride layers and into the SiC substrate, thereby removing all III-N species from the areas between the sidewalls of the resulting seed forms. The latter were rectangular stripes oriented along the $\langle 1\bar{1}00 \rangle$ direction and having widths of 2 and $3\text{ }\mu\text{m}$ and separation distances of 3 and $7\text{ }\mu\text{m}$, respectively.

Pendeoepitaxial growth was achieved at $1050\text{--}1100\text{ }^{\circ}\text{C}$ and 45 Torr. Triethylgallium ($26.1\text{ }\mu\text{mol/min}$) and NH_3 (1500 sccm) precursors were used in combination with a H_2 diluent (3000 sccm). The morphological microstructures have been investigated using scanning electron microscopy (SEM) (JEOL 6400 FE) and atomic force microscopy (AFM) (Digital Instruments Dimension 3000). Defect microstructures and optical characteristics have been investigated using transmission electron microscopy (TEM) (TOPCON 002B, 200 kV) and photoluminescence (PL) [15 mW He-Cd laser ($\lambda = 325\text{ nm}$) excitation source], respectively.

The pendeoepitaxial phenomenon takes advantage of growth mechanisms suggested by Zheleva *et al.*¹⁰ in the conventional LEO technique, and incorporates two additional key ingredients, namely, initiation of growth from a GaN face other than (0001), and the use of the substrate (in this case SiC) as a mask. During the first growth event, GaN selectively grows only on the GaN sidewalls. Common to conventional LEO, no growth occurs on the silicon nitride mask covering the seed structure. Additionally, no growth occurs on the exposed SiC substrate. At the higher growth temperatures employed for enhancing lateral growth, the Ga- and N-containing species are more likely to either diffuse along or evaporate from both the silicon nitride mask and the sili-

FIG. 3. Cross-sectional tunneling electron micrograph of a $1\text{ }\mu\text{m}$ wide GaN seed form oriented along the $\langle 1\bar{1}00 \rangle$ direction, and the GaN pendeoepitaxial layer which has coalesced over the silicon nitride seed mask.

con carbide substrate rather than having sufficient time to form GaN nuclei. The pronounced effect of this can be seen in Fig. 2 where the newly deposited GaN is truly suspended from the sidewalls of the GaN seed form.

The second PE stage, namely, the vertical growth of GaN occurs from the advancing (0001) face of the laterally growing material at a rate that is controlled by the deposition parameters. Extension of vertical growth to a height greater than the silicon nitride mask allows the third growth event, namely, conventional LEO growth, and eventual coalescence over the silicon nitride mask/seed structure assembly to occur.

Atomic force microscopy analysis of the (0001) surface reveals a typical step flow growth mode and a root mean square (rms) roughness of $4.78\text{ }\text{\AA}$. AFM analysis of the $(11\bar{2}0)$ sidewall reveals an atomically smooth surface and a rms roughness of $0.96\text{ }\text{\AA}$. A cross-sectional TEM micrograph showing a discrete pendeoepitaxial structure that has coalesced over the silicon nitride mask is shown in Fig. 3. Threading dislocations, originating from the GaN/AlN and AlN/SiC interfaces and extending into the GaN seed form are clearly visible. The silicon nitride mask acts as a barrier to further vertical propagation of these defects into the pendeoepitaxial film. As the laterally grown GaN is suspended above the SiC substrate, the threading defects associated with the lattice mismatch between GaN/AlN and AlN/SiC cannot extend into this material. Preliminary analysis of the laterally grown GaN reveal horizontal defects which are believed to be stacking faults parallel to the (0001) plane. Optimization of the etching of the GaN seed structure may reduce or eliminate these defects. However, as in the case of LEO, there is a significant reduction in the dislocation density in the lateral growth areas.

Continued PE results in coalescence of the adjacent lateral growth fronts and the formation of a continuous layer of GaN, as observed in Fig. 4. The low-temperature (7 K) PL spectrum of the coalesced PE GaN is shown in Fig. 5. The edge emission band (3.454 eV), assigned to an exciton bound to a neutral donor ($X-D^0$) and is blueshifted (-12 meV) compared to the GaN seed layer, and the commonly seen weak yellow band (2.288 eV) were observed for the pendeoepitaxial layer. The blueshift is attributed to relaxation of the pendeoepitaxial grown GaN using a GaN/AlN/SiC substrate.

In summary, pendeoepitaxy has been developed as a

FIG. 4. Cross-sectional scanning electron micrograph of GaN pendeoepitaxy showing coalescence over and between the seed forms resulting in the formation of a continuous GaN layer.

technique for the growth of GaN films and the latter investigated using SEM, TEM, AFM, and photoluminescence. Incorporation of silicon nitride masks, SiC substrates and etched sidewalls of GaN seed forms has allowed the achievement of films with low dislocation densities over an entire GaN layer. All vertically threading defects stemming from

FIG. 5. Low temperature (7 K) photoluminescence spectrum of a coalesced layer of pendeoepitaxial GaN grown on GaN/AlN/6H-SiC substrate.

the GaN/AlN and AlN/SiC interfaces are contained within the seed forms. Investigations regarding the optimization of growth conditions are ongoing. This approach allows in one regrowth step the near elimination of all threading defects propagating into the pendeoepitaxial GaN layer.

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- ¹S. Nakamura, T. Mukai, and M. Senoh, *Appl. Phys. Lett.* **64**, 1687 (1994).
- ²S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, *Jpn. J. Appl. Phys., Part 2* **35**, L74 (1996).
- ³K. Doverspike, G. Bulman, S. Sheppard, H. Kong, M. Leonard, H. Dieringer, T. Weeks, Jr., J. Edmond, J. Brown, J. Swindle, J. Schetzina, Y. Song, M. Kuball, and A. Nurmikko, *Mater. Res. Soc. Symp. Proc.* **482**, 1169 (1998).
- ⁴R. Underwood, D. Kapolnek, B. Keller, S. Keller, S. Denbaars, and U. Mishra, *Topical Workshop on Nitrides*, Nagoya, Japan, September, 1995.
- ⁵Y. Kato, S. Kitamura, K. Hiramatsu, and N. Sawaki, *J. Cryst. Growth* **144**, 133 (1994).
- ⁶O. Nam, M. Bremser, B. Ward, R. Nemanich, and R. Davis, *Mater. Res. Soc. Symp. Proc.* **449**, 107 (1997).
- ⁷O. Nam, M. Bremser, B. Ward, R. Nemanich, and R. Davis, *Jpn. J. Appl. Phys., Part 2* **36**, L532 (1997).
- ⁸A. Sakai, H. Sunakawa, and A. Usui, *Appl. Phys. Lett.* **73**, 481 (1998).
- ⁹H. Marchand, X. Wu, J. Ibbetson, P. Fini, P. Kozodoy, S. Keller, J. Speck, S. Denbaars, and U. Mishra, *Appl. Phys. Lett.* **73**, 747 (1998).
- ¹⁰T. Zheleva, O. Nam, M. Bremser, and R. Davis, *Appl. Phys. Lett.* **71**, 2472 (1997).
- ¹¹O. Nam, T. Zheleva, M. Bremser, and R. Davis, *Appl. Phys. Lett.* **71**, 2638 (1997).
- ¹²H. Zhong, M. Johnson, T. McNulty, J. Brown, J. Cook, Jr., and J. Schetzina, *MRS Internet J. Nitride Semicond. Res.* **3**, 6 (1998).
- ¹³S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano, and M. Chocho, *Appl. Phys. Lett.* **72**, 211 (1998).
- ¹⁴T. Zheleva, S. Smith, D. Thomson, K. Linthicum, P. Rajagopal, and R. Davis, *J. Electron. Mater.* **28**, L6 (1999).
- ¹⁵T. Weeks, Jr., M. Bremser, K. Ailey, E. Carlson, W. Perry, and R. Davis, *Appl. Phys. Lett.* **67**, 401 (1995).