Nitrides
Indium Gallium Nitride on Germanium by Molecular Beam Epitaxy

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ABSTRACT

Indium containing III-Nitride layers are predominantly grown by heteroepitaxy on foreign substrates, most often Al$_2$O$_3$, SiC and Si. We have investigated the epitaxial growth of In$_x$Ga$_{1-x}$N (InGaN) alloys on Ge substrates. First we looked at the influence of buffer layers between the InGaN and Ge substrate. When applying a high temperature (850 °C) GaN buffer, the InGaN showed superior crystal quality. Furthermore the influence of growth parameters on the structural quality and composition of InGaN layers has been looked into. For a fixed gallium and nitrogen supply, the indium beam flux was increased incrementally. For both nitrogen- as well as for metal (Ga + In) rich growth conditions, the In incorporation increases for increasing In flux. However, for metal rich growth conditions, segregation of metallic In is observed. An optimum in crystal quality is obtained for a metal:nitrogen flux ratio close to unity. The XRD FWHM of the GaN (0002) reflection increases significantly after InGaN growth. Apparently the presence of indium deteriorates the GaN buffer during InGaN growth. The mechanism of the effect is not known yet.

INTRODUCTION

Single crystalline indium containing III-Nitrides show interesting electrical and optical properties. The ability to tune the direct band gap by changing the alloy composition is promising for solar matched photovoltaics. Indium containing III-Nitride layers are predominantly grown by heteroepitaxy on foreign substrates, most often Al$_2$O$_3$, SiC and Si [1,2,3]. This material system is promising for photovoltaic applications [2,3,4,5].

Better understanding of the growth processes is needed to improve the structural and optoelectronic properties. In this work we investigate the heteroepitaxial growth of Indium Gallium Nitride layers on germanium substrates with molecular beam epitaxy (MBE).

Previously we have demonstrated heteroepitaxial growth of GaN on Ge(111) by plasma assisted molecular beam epitaxy (PAMBE) [6]. The use of Ge substrates for III-Nitrides growth, and in particular InGaN, could be advantageous for devices in which vertical conduction is required [7]. A direct photo electrolysis cell, using photocurrent to split H$_2$O into H$_2$ and O$_2$, is an example of a device, which would benefit from vertical conduction. Using a back contact can much simplify such a design. Another promising application of InGaN on conducting Ge substrates is a high-efficiency solar cell. InGaN can absorb the UV and visible part of the solar spectrum and germanium the infrared part.

In this work we report on the influence of buffer layers and growth parameters on the structural quality and composition of InGaN layers grown on Germanium (111) substrates. X-ray
diffraction (XRD) has been used to determine the indium content, crystal quality, the homogeneity and the presence of InN and metallic indium clusters. The surface morphology and layer thickness has been investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

EXPERIMENTAL DETAILS

Germanium substrates with (111) orientation and diameter of 2 inch were chemically cleaned to remove metallic contamination, particles and native oxide from the surface, just before loading into the MBE system. Subsequently, the samples were degassed at 450 °C in vacuum with a background pressure of 1 x 10^{-9} Torr. The cleanliness of the surface was confirmed by reflection high-energy electron diffraction (RHEED), which showed a reconstructed surface. Substrate temperatures were measured by thermocouple. A N\textsubscript{2} flow of 1.2 SCCM and a radio frequency power of 250 W have been used. These settings correspond to an atomic nitrogen beam equivalent pressure of around 4.5 x 10^{-7} Torr or 8.0 x 10^{14} atoms cm^{-2} s^{-1}. A few monolayers of single crystalline Ge\textsubscript{3}N\textsubscript{4} are formed by exposing the substrate to nitrogen plasma at 850 °C [8]. The presence of this crystalline Ge\textsubscript{3}N\textsubscript{4} layer just before the start of GaN growth, has been used to explain the epitaxial growth of GaN on Ge(111) [8]. The indium content has been deduced from the position of the XRD (0002) InGaN reflection, assuming 100 % relaxation. This assumption is reasonable regarding InGaN thicknesses of around 1 micron and lattice mismatches with respect to the underlying GaN from 1.1 to 2.1 %.

DISCUSSION

Influence of buffer layer

First, we have investigated the influence of buffer layers on subsequent InGaN growth: high temperature (HT) GaN (sample A), HT GaN followed by low temperature (LT) GaN (sample B), HT GaN followed by graded InGaN (sample C), graded InGaN (sample D), and finally without any buffer layer (sample E). Following these buffer layers, InGaN is always grown for 90 minutes with a Ga beam equivalent pressure of 3.8 x 10^{-7} Torr. The In beam equivalent pressure is kept at 1.1 x 10^{-7} Torr or is increased in time to 1.1 x 10^{-7} Torr for the graded layers. The high temperature GaN buffer layer is grown at 850 °C by supplying a Ga flux with 1.05 x10^{-6} Torr beam equivalent pressure, just after formation of Ge\textsubscript{3}N\textsubscript{4}. Deposition of GaN at the above mentioned growth parameters leads to the suppression of domain formation in the GaN layer by enhancing step flow growth with respect to 2D nucleation [9]. Substrate temperatures below 850 °C, for the given nitrogen plasma settings, lead to the formation of rotated GaN domains [9]. For this reason, we did not use LT GaN as starting buffer layer. The HT GaN layer thickness is 50 nm (sample A). The second buffer (sample B) that has been investigated is similar to the high temperature GaN, except that a second GaN layer is grown at low temperature. The low temperature GaN buffer has been grown at 450 °C just after HT GaN epitaxy, and is 10 nm thick. As third option a graded InGaN has been grown on a HT GaN buffer (sample C). The graded layer is grown at 450 °C and starts with Ga and In beam fluxes of 4.4 x 10^{-7} Torr and 0 Torr, respectively. During 10 minutes the Ga and In beam fluxes are gradually reduced to 3.8 x 10^{-7} and increased to 1.1 x 10^{-6} Torr, respectively. The graded InGaN layer has a
thickness of about 100 nm. The fourth buffer was a graded InGaN layer grown directly after Ge3N4 formation (Sample D)." 

As reference, InGaN has been grown without buffer layer at 450 °C directly after Ge3N4 formation at 850 °C (sample E). The properties of these InGaN layers, grown with different buffer layers (sample A to E) are summarized in table I.

Table I. Properties of InGaN layers grown with different buffer layers on germanium substrates. The InGaN layers are grown with the same growth parameters (Ga flux, In flux, growth temperature, growth duration).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Buffer</th>
<th>In conc. (%)</th>
<th>Roughness (nm)</th>
<th>XRD ω(0002)FWHM GaN (arc sec)</th>
<th>XRD ωInGaN (arc sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HT GaN</td>
<td>12.4</td>
<td>44</td>
<td>1200</td>
<td>3686</td>
</tr>
<tr>
<td>B</td>
<td>HT + LT GaN</td>
<td>10.2</td>
<td>41</td>
<td>1158</td>
<td>3323</td>
</tr>
<tr>
<td>C</td>
<td>HT GaN + graded InGaN</td>
<td>12.5</td>
<td>65</td>
<td>1221</td>
<td>14009</td>
</tr>
<tr>
<td>D</td>
<td>graded InGaN</td>
<td>16.4</td>
<td>36</td>
<td>9540</td>
<td>7344</td>
</tr>
<tr>
<td>E</td>
<td>/</td>
<td>13.0</td>
<td>28</td>
<td>/</td>
<td>7091</td>
</tr>
</tbody>
</table>

XRD ω-2θscans, measured with a Panalytical X’Pert system, are shown in Fig. 1 (a). From the peaks at 15.7 ° it follows that some InN is present in the InGaN layer or on the InGaN surface. This is notably the case for the HT +LT GaN buffer (sample B) and the InGaN without buffer (sample E). Apparently these conditions lead to In segregation and InN formation. The InGaN and GaN diffraction peaks are situated around 17 ° and 17.3 °, respectively. The layers with graded InGaN buffer (samples C and D) showed as expected a broader InGaN peak, indicating a broader composition variation. When comparing InGaN with HT GaN (sample A) and HT +LT GaN (sample B) we observe a side feature when no LT GaN is used, but a less intense InN peak. This indicates that at the onset of growth more In is incorporated in the InGaN layer and less In segregates for the HT GaN buffer. The InGaN surface roughness is very high and comparable for both samples: more than 40 nm root mean square (RMS) roughness was measured by AFM. A difference in stress in the GaN buffer, could explain these differences. When comparing the XRD rocking curves (ω scan) of the (0002) reflections, Fig. 1 (b), it is clear that the HT GaN and the HT + LT GaN buffers give the best InGaN quality. The InGaN on the HT GaN buffer showed a lower InN peak intensity. For this reason we use this buffer layer further in this work. A thickness of 50 nm has been chosen. This thickness allows measuring the GaN buffer quality with XRD. Thinner GaN buffers can be useful to preserve electrical conduction between the InGaN layer and Ge substrate.
We have investigated the influence of indium flux on the structural quality and indium content of InGaN layers grown on top of the optimized HT GaN buffer. The Ga flux and growth time were kept fixed at a beam equivalent pressure of $3.8 \times 10^{-7}$ Torr and 90 minutes, respectively. The In beam flux was varied from $0.8$ to $1.8 \times 10^{-7}$ Torr. The properties of these samples (A and F to J) are summarized in Table II.

Table II. Properties of InGaN layers grown with different indium fluxes on germanium substrates with 50 nm HT GaN buffer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>In flux $(1 \times 10^{-7}$ Torr)</th>
<th>In conc. (%)</th>
<th>Thickness (nm)</th>
<th>Roughness GaN (nm)</th>
<th>Roughness InGaN (arc sec)</th>
<th>XRD $\omega$ (0002) FWHM GaN (arc sec)</th>
<th>XRD $\omega$ (0002) FWHM InGaN (arc sec)</th>
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</thead>
<tbody>
<tr>
<td>F</td>
<td>0.8</td>
<td>9.7</td>
<td>1076</td>
<td>55</td>
<td>1108</td>
<td>3273</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1.0</td>
<td>11.7</td>
<td>1105</td>
<td>59</td>
<td>1123</td>
<td>3901</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.1</td>
<td>12.4</td>
<td>1020</td>
<td>44</td>
<td>1200</td>
<td>3686</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>1.2</td>
<td>13.4</td>
<td>1172</td>
<td>39</td>
<td>1517</td>
<td>4989</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>1.6</td>
<td>15.2</td>
<td>956</td>
<td>73</td>
<td>1637</td>
<td>3087</td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>1.8</td>
<td>16.9</td>
<td>1280</td>
<td>75</td>
<td>1989</td>
<td>2438</td>
<td></td>
</tr>
</tbody>
</table>

For both nitrogen (F) as well as metal (Ga+In) rich (H to J) growth conditions the indium incorporation increases linearly for increasing indium flux, as shown in Fig. 2 (b). However, for metal rich growth conditions segregation of metallic indium occurs as evident by the presence of a diffraction peak at 16.4°. An optimum in X-ray diffraction intensity is obtained for a Ga+In to N flux ratio close to unity, with indium beam equivalent pressure of $1.0-1.1 \times 10^{-7}$ Torr.
Figure 2: (a) XRD ω-2θ scans for InGaN layers grown with different indium fluxes. (b) In content measured from XRD and XRD peak intensity in function of indium flux.

The thickness and root mean square (RMS) roughness have been measured by SEM and AFM, respectively. A surface area of 1.0 by 1.0 micron was scanned by AFM. All layers are quite rough, see Fig. 3 (a) and (b).

Figure 3: (a) SEM images of sample A, showing columnar InGaN. (b) AFM measurement of sample A, showing a rough surface.

The XRD FWHM of the GaN (0002) reflection increases significantly after InGaN growth. Without InGaN layer a FWHM of the (0002) reflection of 410 arc sec is obtained. When InGaN is grown on the GaN buffer, a FWHM of 1200 arc sec is measured. Apparently the GaN layer deteriorates during subsequent InGaN growth. The mechanism of the effect is not known at this time. Further investigation by transmission electron microscopy (TEM) would be interesting.
CONCLUSIONS

InGaN layers have been grown by molecular beam epitaxy on various substrates. When using Ge(111) substrates, a 50 nm thin GaN buffer layer grown at high temperature seems the best option. The influence of indium flux on the structural quality, surface morphology and indium content has been investigated. For both nitrogen as well as metal (Ga+In) rich growth conditions the indium incorporation increases for increasing indium flux. However, for metal rich growth conditions segregation of metallic indium is observed. An optimum in crystal quality is obtained for a Ga+In to N flux ratio close to unity, with an indium beam equivalent pressure of 1.0-1.1 x 10^{-7} Torr. The XRD FWHM of the GaN (0002) reflection increases significantly after InGaN growth. Apparently the presence of indium deteriorates the GaN buffer during InGaN growth. The mechanism of the effect is not known yet. Intermixing of the InGaN layer and GaN buffer, trough the presence of defects, is a possibility.

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REFERENCES

Crack-free III-nitride structures (> 3.5 μm) on silicon

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ABSTRACT

III-nitride structures on Si are of great technological importance due to the availability of large area, epi ready Si substrates and the ability to heterointegrate with mature silicon micro and nanoelectronics. High voltage, high power density, and high frequency attributes of GaN make the III-N on Si platform the most promising technology for next-generation power devices. However, the large lattice and thermal mismatch between GaN and Si (111) introduces a large density of dislocations and cracks in the epilayer. Cracking occurs along three equivalent {11-100} planes which limits the useable device area. Hence, efforts to obtain crack-free GaN on Si have been put forth with the most commonly reported technique being the insertion of low temperature (LT) AlN interlayers. However, these layers tend to further degrade the quality of the devices due to the poor quality of films grown at a lower temperature using metal organic chemical vapor deposition (MOCVD). Our substrate engineering technique shows a considerable improvement in the quality of 2 μm thick GaN on Si (111), with a simultaneous decrease in dislocations and cracks. Dislocation reduction by an order of magnitude and crack separation of > 1 mm has been achieved. Here we combine our method with step-graded AlGaN layers and LT AlN interlayers to obtain crack-free structures greater than 3.5 μm on 2” Si (111) substrates. A comparison of these film stacks before and after substrate engineering is done using atomic force microscopy (AFM) and optical microscopy. High electron mobility transistor (HEMT) devices developed on a systematic set of samples are tested to understand the effects of our technique in combination with crack reduction techniques. Although there is degradation in the quality upon the insertion of LT AlN interlayers, this degradation is less prominent in the stack grown on the engineered substrates. Also, this methodology enables a crack-free surface with the capability of growing thicker layers.

INTRODUCTION

Growth of nitrides on silicon has gained tremendous interest over the past decade. The large scale availability, low cost, and high quality of the Si substrates combined with the large bandgap, high breakdown strength, high maximum oscillation frequency, superior noise factor, and high current attributes of GaN, makes this platform very attractive for next generation devices. The major roadblock with realizing this is the large difference in thermal expansion coefficients (χSi = 2.59×10⁻⁶ K⁻¹ and χGaN = 5.59×10⁻⁶ K⁻¹) and lattice constants (aSi(111) = 3.84 Å and aGaN = 3.189 Å) between the two material systems [1, 2]. This leads to a large density of cracks in the epilayer along three equivalent {11-100} planes and dislocations around 10¹⁰ cm⁻².
Strain management techniques have been incorporated for the reduction and elimination of cracking over a large area, with the commonly used methods being LT AlN interlayers [5], AlN/GaN superlattices [6] or AlGaN/GaN superlattices [7], and graded AlGaN buffers [8]. However, a simultaneous reduction in dislocations in conjunction with the above mentioned methods has still remained a challenge.

We have developed a technique to modify the Si substrate by implantation of nitrogen ions through a high temperature (HT) AlN wetting layer into the substrate. This method has demonstrated a simultaneous and considerable reduction in cracking and dislocation defects. Crack separation of greater than 1 mm and dislocation reduction down to \(10^8\) cm\(^{-2}\) has been achieved in a 2\(\mu\)m thick GaN grown on Si [9, 10]. Here we combine our method with commonly used strain reduction techniques to obtain crack-free structures over a 2" wafer. The purpose of this study is to take advantage of the improved GaN quality resulting from the substrate engineering technique and also create thicker crack-free layers. This is necessary to reduce vertical leakage and also provide greater electrical isolation from the substrate, required for devices like HEMTs. Various AlGaN/GaN HEMT devices are developed and the impact of combining our substrate engineering technique with other crack reducing methods is explored.

**EXPERIMENT**

Deposition of AlN buffers on 2" Si (111) substrates is done at a temperature of about 1010 °C using a Veeco D180 MOCVD (metal organic chemical vapor deposition) reactor. The details of sample preparation prior to growth are listed elsewhere [11]. Some of these samples undergo our substrate engineering process before regrowth. This involves the implantation of nitrogen at energy of 65 keV and a dose of \(2\times10^{16}\) cm\(^{-2}\) through the AlN/Si stack to create an amorphized region within Si beneath the AlN-Si interface.

To develop crack-free structures greater than 3.5 \(\mu\)m, engineered AlN/Si substrate and un-treated AlN/Si substrates are used. Both types of samples underwent in-situ annealing for 30 minutes in \(N_2\) prior to the growth of a step-graded Al\(_{x}\)Ga\(_{1-x}\)N buffer layer. The step-graded buffer consisted of decreasing Al percentages of 75%, 66%, 50%, 33%, and 20%, with each Al\(_{x}\)Ga\(_{1-x}\)N layer 100 nm thick. 1\(\mu\)m GaN is grown on top of this buffer followed by three LT AlN interlayers (each 15 nm thick) separated by 250 nm of GaN. This is then followed by growth of 1.5 \(\mu\)m of GaN.

Four HEMT devices are fabricated on Si: (1) Sample A: without LT AlN interlayers, (2) Sample B: with LT AlN interlayers, (3) Sample C: engineered substrate without LT AlN interlayers, and (4) Sample D: engineered substrate with LT AlN interlayers. Figure 1 shows a schematic of the HEMT device.

On-wafer characterizations including optical microscopy, AFM, and low temperature (LT) photoluminescence (PL) are performed. LT PL measurements are performed at 8 K using a He-Cd 325 nm laser source. Above mentioned thick 3.5 \(\mu\)m structures are compared to our standard 2 \(\mu\)m of GaN on engineered substrate that does not have a step-graded AlGaN buffer and LT AlN interlayers. Moreover, HEMT on Si structures were processed/fabricated and measured and are compared amongst each other and also with a similar HEMT structure grown on sapphire.