Nitride light-emitting diodes grown on Si (111) using a TiN template

N. C. Chen, W. C. Lien, C. F. Shih, and P. H. Chang
Institute of Electro-Optical Engineering, Department of Electronic Engineering, Chang Gung University,
Tao-Yuan 333, Taiwan, Republic of China

T. W. Wang and M. C. Wu
Institute of Electro-Optical Engineering, National Tsing-Hua University, Hsinchu 30013, Taiwan,
Republic of China

(Received 8 November 2005; accepted 22 March 2006; published online 10 May 2006)

Nitride light-emitting diodes (LEDs) are grown on a Si (111) substrate with a TiN template. Transmission electron microscopy and x-ray diffraction indicate that the epitaxial relation follows Si(1,1,1)∥TiN(1,1,1)∥AlN(0,0,1), Si[1,1,0]∥TiN[1,1,0], and Si[0,0,1]∥TiN[0,0,1]. The reflectance measurement and simulation results indicate that the TiN can be adopted as a reflector to mitigate the substrate absorption problem, thus increasing the extraction efficiency of nitride LEDs grown on Si. © 2006 American Institute of Physics. [DOI: 10.1063/1.2202389]

Group-III nitride semiconductors have been extensively investigated in recent years. A band gap in the range of 0.7–6.2 eV with direct optical transition makes this material appropriate for optical electronics with application from infrared to ultraviolet. Light-emitting diodes (LEDs) currently represent the most important application for this material. The enhancement of light-emitting efficiency means that GaN grown on sapphire or SiC substrates. The cost and small size of these substrates inhibit the progress of solid-state lighting technology. To overcome these problems, many attempts have been made to apply silicon as the substrate for nitride epitaxy. Silicon substrate has many benefits over sapphire, such as large wafer size, low cost, conduction, high thermal conductivity, and mature processing technique. Despite the large difference between thermal expansion coefficients of III-nitride and silicon, several researchers have demonstrated nitride LEDs grown on silicon.

However, adopting the silicon substrate still presents some difficulties. For example, the extraction efficiency is limited by the substrate absorption. Moreover, the group V gas source NH3 reacts easily with the substrate to form amorphous SiN, disrupting the nitride epitaxy. AlN with an Al-predeposition layer is usually used as the nucleation layer to suppress this parasitic reaction. The operating voltage of a vertical-conducting LED is increased to compensate the high resistivity of AlN and the large band offset between AlN and Si. Therefore, a reflective, conductive, and small lattice-mismatched nucleation layer is desired when employing silicon as the substrate.

The application of rocksalt-type titanium nitride has previously been studied. This material has recently been employed as gate electrodes in field-effect transistors, and in advanced metallization schemes for ultralarge scale integrated applications for Si-based devices. Additionally, TiN has been revealed to form good Ohmic (rectifying) contact with n-type (p-type) GaN. However, this material is seldom used for III-nitride epitaxy. Oshima et al., Tavemier et al., and Fu et al. had evaporated a titanium layer on GaN grown on sapphire. This metal layer formed a native nanomask after nitridating this layer under NH3 environment at a high temperature. A very thick GaN layer was grown on the nanomask, forming void between the nanomask and the GaN grown subsequently. Thereafter, high quality and freestanding GaN substrates could be easily obtained by the void-assisted separation method. Watanabe et al. had explored a possibility of growing GaN on sapphire with a TiN buffer layer. They found that the choice of the N2/(N2+Ar) ratio during TiN deposition and nitridating the TiN buffer layers after TiN deposition were essential to grow continuous, flat GaN layers. Another related study had been reported by Armitage et al. They successfully grew GaN on both the (111) and (001) Si surfaces with the lattice-matched HfN buffer layers. No other works have been published on the performance enhancement of nitride LED grown on silicon with the help of TiN. However, TiN has some potential benefits when adopted as a template. First, the shining yellowish color of this material manifests itself as a reflector to increase the extraction efficiency. Second, this material has high conductivity. Third, the lattice mismatch between TiN (111) (α=0.2998 nm) and AlN (001) (α=0.3111 nm) and TiN and GaN (001) (α=0.3189 nm) are as small as 3.7% and 6.3%, respectively.

In this study, a preferred TiN (111) film with a thickness of 50 nm on Si (111) was grown by a direct current magnetron sputtering system with a base pressure of 1.5×10−6 mbar. The total pressure (Ar+N2) was maintained at 3×10−3 Torr during sputtering with 3% nitrogen fraction at 600 °C. Figure 1(a) shows the reflectance of our TiN sample and a bare silicon. The reflectance of the TiN sample increased monotonically with the wavelength, as revealed by the equation,

$$R = \frac{(n_2 - n_1)^2 + (\kappa - \kappa_1)^2}{(n_2 + n_1)^2 + (\kappa + \kappa_1)^2},$$

where R is the reflectivity, n is the refractive index, κ is the extinction coefficient, and the subscripts 1 and 2 denote air and the reflective material, respectively. For silicon, κ=0 in the wavelength range of 450–900 nm. Therefore, the reflectance of the air/Si interface was dominated by the difference between the refractive indices. However, the reflectance was
dominated by the difference of the extinction coefficients for the air/TiN interface. The $\kappa$ value of TiN rose monotonically from 1 to 4 in the wavelength range of 450–900 nm, explaining the increase in the reflectance of the TiN sample with rising wavelength, and the sample’s shining yellow. The penetration depth of light (wavelength/2$\pi\kappa$) was less than 100 nm owing to the large extinction coefficient, the light reflected from the TiN/Si interface did not interfere with the light reflected from the air/TiN interface in our case, and so the effect of the underlying Si on reflection could be ignored. Furthermore, the reflectance of the air/Si interface was apparently larger than that of the air/TiN interface between 450 and 480 nm. However, the light in a LED is not generated from air, but instead from the quantum wells within the GaN. Therefore, the $n$ and $\kappa$ values of air should be replaced by the parameters of the GaN. The inset of Fig. 1(a) illustrates the simulation results. This figure indicates that the reflectance of the GaN/TiN interface was larger than that of the GaN/Si interface at all wavelengths. For instance, inserting a TiN layer at 450 nm increased the reflectivity from 9% to 25%.

A low-temperature (LT) AlN layer (20 nm), a high-temperature (HT) AlGaN layer (100 nm), a LT-AlN interlayer (15 nm) inserted in HT-GaN (1 $\mu$m),$^{20}$ three InGaN quantum wells (MQWs), and a $p$-GaN layer (100 nm) were later grown on the sample in sequence by metal-organic chemical vapor deposition (Axitron 200-4/RF-S). Details of the growth procedure are similar to Ref. 8. The solid line in Fig. 1(b) shows the reflectance result of the epilayer, and the dashed line shows the simulation result from the structure grown in this experiment. The simulation was found to describe the reflectance accurately. The dotted line indicates the simulation result after the TiN layer was removed. This plot also indicates that inserting TiN can substantially increase the reflectivity of the underlying interface.

Figure 2 displays the cross-sectional images of the Si/TiN/AlN/AlGaN interfaces observed by high-resolution transmission electron microscopy (HR-TEM). The x-ray diffraction (XRD) $\theta/2\theta$ pattern, depicted in the inset of Fig. 2(a), shows that the TiN(111), AlN (002), and GaN (002) faces are parallel to the Si(111) face. The selected area electron diffraction (SAED) pattern of the Si/TiN/AlN interface, depicted in another inset of Fig. 2(a), confirms that the epitaxial relations follow $\text{Si}(111)\parallel\text{TiN}(111)\parallel\text{AlN}(002)$, $\text{Si}(111,0)\parallel\text{TiN}[1,1,0]\parallel\text{AlN}[0,0,1]$, and $\text{Si}[0,0,1]\parallel\text{TiN}[0,0,1]$. Figures 2(b) and 2(c) show the lattice images of the Si/TiN and TiN/AlN/AlGaN interfaces, respectively. The large lattice mismatch between TiN (111) and Si (111) can be eliminated by introducing a periodic array of misfit dislocations, as shown in Fig. 2(b). In this case, the distance of about four {111}$_\text{Si}$ planes was found to correspond to that of five
put efficiency of the LED with TiN layer is about 10% higher than the one without TiN, thus confirming the enhancement of the extraction efficiency. The other differences are still under study.

In conclusion, nitride LEDs were grown on Si (111) substrate with a TiN template. The measurements of TEM and XRD indicate that the epitaxial relation followed $\text{Si}(1,1,1)\parallel\text{TiN}(1,1,1)\parallel\text{AlN}(0,0,1)$, $\text{Si}(1,1,0)\parallel\text{TiN}(1,1,0)$, and $\text{Si}(0,0,1)\parallel\text{TiN}(0,0,1)$. The results of reflectance indicate that TiN can be adopted as a reflector to ease the substrate absorption problem and therefore improve the extraction efficiency for nitride LEDs grown on Si. Moreover, the high conductivity of TiN indicates that it can be used to develop vertical light-emitting devices over Si substrate.

The authors would like to thank the National Science Council of Taiwan, Republic of China for financially supporting this research.

TABLE I. FWHM of x-ray diffraction. The unit is arc sec.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\theta$–$2\theta$</th>
<th>Rocking curve</th>
<th>$\theta$–$2\theta$</th>
<th>Rocking curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>With TiN</td>
<td>214</td>
<td>1547</td>
<td>3100</td>
<td>4519</td>
</tr>
<tr>
<td>Without TiN</td>
<td>221</td>
<td>1552</td>
<td>3475</td>
<td>4034</td>
</tr>
</tbody>
</table>

{111}$\text{TiN}$ planes, which is consistent with the theoretical lattice mismatch of around 20%. Only little misfit dislocations were found near the abrupt TiN/AlN interface [Fig. 2(c)].

Figure 3(a) shows the picture of a LED made from the epiwafer studied herein at a forward current of 1 mA. The only significant features in this figure are some crack lines resulting from the different thermal expansion coefficients of nitride and Si. Figure 3(b) shows the spectrum of this chip, in which the peak wavelength was 474 nm and the full width at half maximum (FWHM) was 25 nm. The FWHM is similar to other chips grown on Si without TiN. Therefore, the underlying TiN layer does not degrade the quality of the nitride epilayer.

To further investigate the influence of the TiN on the crystal quality and on the LED performance, another sample grown at the same condition but without the TiN layer had been prepared. The data of x-ray diffraction shown in Table I demonstrate that the quality of the nitride epilayer was not degraded by the insertion of the TiN. Besides, the light output efficiency of the LED with TiN layer is about 10% higher than the one without TiN.