Plasma-assisted MBE of GaN pn-junction Grown on Si(111) Substrate

Mohd Zaki Mohd Yusoff\textsuperscript{a-b*}, Zainuriah Hassan\textsuperscript{a*}, Chin Che Woei\textsuperscript{a}, Haslan Abu Hassan\textsuperscript{a}

\textsuperscript{a}. Nano-Optoelectronics Research and Technology Laboratory, School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia
\textsuperscript{b}. Department of Applied Sciences, Universiti Teknologi MARA, 13500 Permatang Pauh, Penang, Malaysia

(Dated: Received on March 11, 2010; Accepted on June 1, 2010)

We investigated growth of GaN pn-junction layers grown on silicon(111) by plasma-assisted molecular beam epitaxy system and its application for photo-devices. Si and Mg were used as n- and p-dopants, respectively. The reflection high energy electron diffraction images indicated a good surface morphology of GaN pn-junction layer. The thickness of GaN pn-junctions layers was about 0.705 nm. The absence of cubic phase GaN showed that this layer possessed hexagonal structure. According to XRD symmetric rocking curve $\omega/2\theta$ scans of (0002) plane at room temperature, the full width at half-maximum of GaN pn-junction sample was calculated as 0.34$^\circ$, indicating a high quality layer of GaN pn-junction. Surprisingly, there was no quenching of the A$_1$(LO) peak, with the presence of Si- and Mg-dopants in sample. The pn-junctions sample has a good optical quality which was measured by the photoluminescence system. For photo-devices applications, Ni and Al were used as front and back contacts, respectively. The current-voltage characteristics of the devices showed the typical rectifying behavior of heterojunction. The photo-current measurement was performed using a visible-lamp under forward and reverse biases. From the temperature-dependent measurements, the current at low bias exhibited much stronger temperature dependence and weaker field dependence. The effect of thermal annealing on front contact Ni was also carried out. The front contact Ni was annealed at 400 and 600 $^\circ$C for 10 min in the nitrogen ambient. The results showed that 600 $^\circ$C treated sample had a higher gain at 1.00 V/e than 400 $^\circ$C treated and untreated samples.

Key words: III-nitrides, GaN, pn-junction, Molecular beam epitaxy, Photodetector

I. INTRODUCTION

Recently, gallium nitride (GaN) and its related compounds involving Al and In have attracted much attention because of their potential being used as high-efficiency UV light emitting devices and high frequency and power electronic devices [1–3]. These materials have exhibited large direct band gap energy, high peak electron velocity, high-saturation velocity, and high breakdown electric field which are considered useful parameters for the above applications [4]. Consequently, the growth and physics of GaN-based materials have received remarkable scientific attention.

The pn-junctions are of great importance both in modern electronic applications and in understanding other semiconductor devices. The pn-junction theory serves as the foundation of the physics of semiconductor devices. The basic theory of current-voltage characteristic of pn-junctions was established by Shockley [5]. This theory was then extended by Sah et al. [6] and Moll [7]. GaN pn-junction grown on silicon substrates have been the focus in a number of recent reports [8–12], and further effort is still necessary to improve its crystalline quality for practical applications.

Photoconductive GaN detectors attracted much interest because of their simplicity and high responsivity, which would enable their use without any preamplifier stage. A very slow non-exponential transient response and poor sensitivities are some of the drawbacks using the AlGaN alloy to make a photodetector. All these problems can be overcome by detectors based on GaN pn-junctions and Schottky barriers. The GaN Schottky barrier and pn-junction photodetectors offer a high speed, and sharp visible cut-off makes them excellent candidates for commercial UV devices.

Silicon substrate presents the obvious advantages of a well-known technology, low cost, and potential hybrid integration. However, Si(111) has been less investigated than sapphire as a substrate to grow nitrides, due to the higher lattice and thermal expansion coefficient mismatches which produce a higher dislocation density and the potential generation of crack [13]. In addition, the

* Authors to whom correspondence should be addressed. E-mail: mzmmy83@gmail.com, zai@usm.my, Tel.: +604-6533673, FAX: +604-6579150

DOI:10.1088/1674-0068/23/04/431-436 431 ©2010 Chinese Physical Society
problems of the interdiffusion at the Si/epilayer interfaces make the interpretation of electrical measurements more difficult [14].

In Ref.[15], X-ray diffraction (XRD) pattern showed that full width at half maximum (FWHM) of AlN(0002) peak grown on Si(111) substrates was smaller than that grown on Si(100) substrates [15]. XRD results also indicated that the preferred orientation of AlN films on Si(111) substrate is more easily controlled than that on Si(100) substrates. It can be attributed to the more matched lattice template with hexagonal structures of AlN films provided by Si(111) plane of silicon [15]. The lattices in AlN(0001) and Si(111) are both hexagonal, and thus Si(111) can provide matched template for AlN(0001) plane. The lattice mismatch between these two planes is only 19%. However, the lattice in Si(100) is square, which is unmatched with hexagonal lattice in AlN(0001) plane. The lattice mismatch between AlN(0001) and Si(100) is 42.7%. The larger lattice mismatch between AlN(0001) and Si(100) is a main contribution to the larger strain in the formed films. In the case of GaN layers grown on AlN buffer layer, the crystallinity quality is much improved because the lattice mismatch between GaN and AlN which is only 2.5% [16]. For these reasons, the Si(111) substrate was used.

In this work, the microstructure and optical properties of GaN pn-junction on AlN/Si(111) substrate grown by plasma-assisted molecular beam epitaxy (MBE) were studied. Scanning electron microscopy (SEM) and high-resolution X-ray diffraction (HR-XRD), Raman spectroscopy and photoluminescence (PL) were used to investigate cross-section and crystalline quality of the heterostructure, respectively. Finally, GaN pn-junction was fabricated by making an ohmic contact on both p-GaN and silicon substrate, respectively. The visible-lamp was also used to measure the photo-current response of devices. The Signatone S-1043 Hot Chuck system was used to study the temperature-dependence of samples. Lastly, the effect of thermal annealing treatments on front contact samples Ni was investigated by using vacuum furnace tube at 400 and 600 °C in nitrogen ambient.

II. EXPERIMENTS

A sample was grown by Vecco Gen II RF PA-MBE system, with silicon and magnesium as n-type and p-type sources, respectively. High purity material sources such as gallium (7N), aluminum (6N5), and indium (7N) were used in the Knudsen cells. Nitrogen with 7N purity was channeled to radio frequency (RF) source to generate reactive nitrogen species. The plasma was operated at typical nitrogen pressure of 2 µPa under a discharge power of 300 W. The growth of III-nitrides on 3-inch Si(111) substrate has started with the standard cleaning procedure by using RCA method. The substrate was then mounted on the wafer holder and loaded into the MBE system. Then Si substrate was heated at 900 °C, and a few monolayers of Ga were deposited on the substrate for the purpose of removing the SiO₂ by formation of GaO₂. Reflection high energy electron diffraction (RHEED) showed the typical Si(111) 7×7 surface reconstruction pattern with the presence of prominent Kikuchi lines, indicating a clean Si(111) surface. Before the growth of nitride epilayers, a few monolayers of Al were also deposited on the Si substrate to avoid the formation of Si₃N₅ which is deleterious for the growth of the subsequent epilayers.

GaN pn-junction was grown by RF plasma-assisted molecular beam epitaxy (PA-MBE) on Si(111) substrate. The buffer or wetting layer, AlN was first grown on the Si substrate. To grow AlN buffer layer, the substrate temperature was heated up to 870 °C, both of the Al and N shutters were opened simultaneously for 15 min. Subsequently, n-GaN epilayer was grown on top of the buffer layer followed by p-GaN epilayer. Both pn-junction layers were grown for 45 min with substrate temperature set at 870 °C, respectively (see Fig.1). For GaN pn-junction layers, silicon and magnesium were used as n and p dopants, respectively. In order to make GaN pn-junction photodetector on silicon, ohmic contact has been fabricated. Ohmic contacts were made by thermal evaporation of Ni and Al on p-GaN and silicon substrate, respectively. The visible lamp was used as a light source for photo-current measurement.

The optical properties studies were performed using HR-XRD, Raman spectroscopy, and PL. The microstructure of a sample was measured by cross-section of SEM. The temperature-dependent measurement was carried out by using Signatone S-1043 Hot Chuck system. The vacuum furnace tube was used to investigate the effect of thermal annealing on front contact sample Ni for 10 min in nitrogen ambient. The back contact Al was deposited after the completion of thermal treatment.

III. RESULTS AND DISCUSSION

Figure 2 shows the RHEED images of sample during the growth of GaN pn-junctions on silicon substrate. The Si substrate surface showed a clear 7×7
FIG. 2 RHEED pattern for the growth process of GaN pn-junction layers on AlN/Si(111). (a) Ga cleaning, (b) AlN, and (c) GaN.

FIG. 3 Cross-sectional SEM image showing the GaN/AlN layers on Si(111) with GaN thickness of 709.5 nm and AlN thickness of 95.5 nm.

FIG. 4 XRD spectra of GaN pn-junctions on Si(111).

surface reconstructions at high temperature, as shown in Fig.2(a). After the growth of AlN, RHEED displayed a streaky pattern indicating good surface morphology as revealed in Fig.2(b). During the last step of GaN pn-junctions growth (Fig.2(c)), the streaky RHEED pattern is sharpened, suggesting the improvement of the crystalline quality of GaN pn-junctions relative to the AlN buffer layer.

Figure 3 shows SEM images of GaN and AlN layers on a Si(111). Both of the layers show good uniformity with an average thickness of about 709.5 nm and 95.5 nm for GaN and AlN layers, respectively. A high-quality heterointerface without cracking were obtained by optimizing the growth conditions.

Figure 4 indicates the 2θ XRD spectra of the sample. The XRD measurement shows that the heterostructure of III-nitrides was epitaxially grown on silicon substrate. It can be seen from the presence of the peak at 34.515° which is identified as wurtzite GaN (0002) diffraction, and three peaks at 36.028°, 72.846°, and 76.503°, which correspond to AlN(0002), GaN(0004), and AlN(0004) respectively. The peak at 28.245° is from the Si(111). The XRD spectra indicate that no sign of cubic phase of GaN is found within the detection limit of the XRD, so it is confirmed that our samples possessed hexagonal structure.

XRD symmetric rocking curve \( \omega/2\theta \) scans of (0002) plane at room temperature was also conducted to verify the crystalline quality of thin films. The full width at half-maximum (FWHM) is the difference between the energies or frequencies on either side of a spectral line or resonance curve at which the line absorption or emission or the resonant quantity reaches half its maximum intensity. According to Fig.5, the FWHM of GaN pn-junction sample was calculated as 0.34°, indicating a high quality of GaN pn-junction layer grown on AlN/Si(111) substrate.

Figure 6 shows the Raman spectrum for the GaN pn-junctions grown on Si(111). The maximum intensity at 523.63 cm\(^{-1}\) is attributed to crystalline silicon. It was found that all the allowed Raman optical phonon modes...
FIG. 6 Room temperature Raman spectrum of GaN pn-junctions on Si(111).

of GaN, i.e. the $E_2$(low), $E_1$(high), and $A_1$(LO) are clearly visible, which are located at 147.76, 571.65, and 737.9 cm$^{-1}$, respectively. The presence of $E_1$(high) has led to the evidence of hexagonal-phase character for this GaN pn-junction layer [17]. For pn-junction sample, it is clearly seen that the effect of the Si- and Mg-dopants has resulted in no quenching of the $A_1$(LO) peak. The $\sim$657.73 cm$^{-1}$ mode was observed from our measurement, which is in agreement with the previous reports [18, 19]. The samples showed p-type conductivity without any post-treatment, as compared with the MOVPE reactor samples [20]. Demangeot et al. suggests that the presence of LO mode in the spectrum indicated the sample had a high crystalline quality. Moreover, the result also proved that this sample had a high carrier concentration [21]. This can be seen from the presence of the peak at 657.73 cm$^{-1}$. The 657.73 cm$^{-1}$ peak is assigned to the local vibrational mode (LVM) for the Mg–N bond which agrees with Harima et al. [22]. This peak is almost the same as the results of Kaschner et al. [23] which also presented native p-type character in their sample. Therefore, it is not surprising that the 657.73 cm$^{-1}$ peak was observed in this sample.

PL measurement was performed at room temperature by using Jobin Yvon HR800UV system with He-Cd laser 325 nm as excitation source. The sample obtained at room temperature shows the band-edge (BE) emission at 358.32 nm ($E_g=hc/\lambda\approx1239.8193$ eV/\(\lambda\approx3.46\) eV) as shown in Fig.7, which is in agreement with that reported by Ponce et al. [24]. The absence of yellow band emission in our PL result confirmed that the thin film is of good optical quality. Furthermore, the absence of hydrogen element during growth was also believed to produce no yellow luminescence in this sample [25]. Unfortunately, there are no significant peaks at $\sim$369 and $\sim$391 nm, which can be related to the shallow donor-acceptor pair transitions [26].

Figure 8 shows the current voltage ($I$-$V$) characteristics of GaN pn-junction photodetector under dark and visible illumination conditions, operating under forward bias. The GaN pn-junction shows a typical rectifying behavior under forward bias. A small deviation responses between photo and dark currents might be due to some defects occurred between buffer layer and silicon. GaN is known to suffer from a high amount of defect densities due to reason like the difference between the thermal expansion coefficient and large lattice mismatch between the substrates and the GaN material, especially of those grown on Si [27–30]. The high amount of dark current observed can be attributed to the tunneling of carrier across the barrier. This effect can be assisted by the interfacial layer to produce trap-assisted tunnel currents. The existence of a thin interfacial layer can not be ruled out unless the semiconductor is cleaved in an ultra-high vacuum condition [31, 32].

The reverse-bias $I$-$V$ characteristics of the diodes on GaN pn-junction were recorded as a function of temperature by placing the sample on a heated chuck during the measurements. The temperature-dependent data, presented in Fig.9, shows the current at low bias exhibits much stronger temperature dependence and weaker field dependence. Kozodoy et al. suggests that thermionic emission over a barrier dominates at this low bias condition [33]. This barrier most likely corresponds to emission from a deep trap level into the band [33]. The increase in thermionic current with increasing bias
FIG. 9 *I*-*V* characteristics of GaN pn-junction grown on AlN/Si substrate at various temperatures.

FIG. 10 Dark current of GaN pn-junction grown on AlN/Si substrate with different thermal annealing for 10 min. is indicative of the Frenkel-Poole field induced barrier lowering effect [34].

In order to investigate the effect of thermal annealing on front contact Ni 400 and 600 °C was chosen. All the samples were annealed in nitrogen ambient for 10 min. Back contact Al was deposited after the thermal treatment on the samples completed. Figure 10 shows dark *I*-*V* characteristics of GaN pn-junction with different thermal annealing temperature on Ni contact for 10 min. It can be seen that the thermal annealing changes the dark currents of the pn-junction structures. This treatment also changes the light currents which were not shown here. More specifically, the thermal treatment increased the dark currents from the zero bias to 5 V for 400 °C treated sample. However, for 600 °C treated sample, the dark increased to 4 V only and then continued to decrease. Results are shown in Fig.10 which suggest that the diffusion of Ni metal layer into the sample away from the GaN surface resulted in a degraded metal-semiconductor contact for the sample under thermal annealing treatment. The differences of thermal expansion coefficient between the Ni (α≈13.4×10⁻⁶ K⁻¹) [35] and GaN (α≈6×10⁻⁶ K⁻¹) [36] might contribute the compressive stress and strain during the heating process as well as the cooling down process to room temperature after annealing [37]. These effects were believed to produce a high dark current level. Moreover, the presence of defects in the sample also might be participated to increase the dark current of sample.

In addition to the *I*-*V* characteristics, the ratio of detector light current to dark current, i.e., gain=light/dark, is often quoted for performance evaluation as an optically controlled electronic switch. Figure 11 shows higher gain compared with other annealing temperature. Generally, we found that thermal annealing treatment resulted in significant changes in the gain factor compared with samples without thermal annealing treatment. Thermal treatment increased the gain factor from zero bias until to 1.8 V only, and then continued to decrease. The higher gain has been recorded as 910 at 1.00 V/e for 600 °C treated sample.

IV. CONCLUSION

The growth of GaN pn-junction on Si(111) substrate has been successfully performed using plasma-assisted molecular beam epitaxy. The microstructure and optical properties of a material has been revealed by using SEM, XRD, Raman, and PL. The sample was grown on a Si(111), showing promising candidate in the fabrication of photo-devices. Temperature-dependent measurements show the stronger temperature dependence and weaker field dependence at low bias voltage. The effect of thermal annealing on front contact Ni indicated that the 600 °C treated sample had higher gain which was recorded as 910 at 1.00 V/e than 400 °C treated and untreated samples.

V. ACKNOWLEDGMENT

This work was supported by the Universiti Sains Malaysia for USM-RU-PRGS (No.1001/PFIZIK/843031).

DOI:10.1088/1674-0068/23/04/431-436