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Abstract
The ineffective p-type doping of nitrides using magnesium (Mg), the best available dopant, has limited the development and performance of all III-nitride-based devices, including bipolar junction transistors and light emitting diodes (LEDs). For nitride-based ultraviolet (UV) LEDs, as the Al composition increases for achieving shorter wavelengths (e.g. <280 nm) into the UVC spectral range, the p-type doping issue, which causes very inefficient hole injection, becomes more severe than ever. In this work, we report the detailed study of using p-type Si as a hole supplier for high-Al composition UVC LEDs. We first describe the method of Si/GaN junction formation, where the lattice-mismatch challenge between Si and GaN is overcome by using a 0.5 nm thick Al2O3 layer at the interface. This serves as a physical separation layer between the two materials as well as a passivation, tunneling, and thermal buffer layer. High-resolution transmission electron microscope image illustrates the high-quality interface between Si and GaN. We further detail the hole transport mechanism of the p–p Si/GaN isotype junction through both simulations and experiments. The enhanced hole concentration in the AlGaN/AlN multiple quantum wells (MQWs) due to the use of p-type Si as the hole supplier is verified through comparison with conventional UVC LEDs. Finally, high-performance UVC LEDs made with AlN/AlGaN (Al: 72%) MQWs employing p-type Si as their hole suppliers are demonstrated experimentally to serve as an example of the novel hole injector strategy.

1. Introduction
A fundamental limitation of III-nitride materials, particularly the nitrides with a high Al content, for junction type devices (e.g. light emitting diodes (LEDs) and bipolar junction transistors) is their ineffective p-type doping. Using magnesium (Mg), the best p-type dopant, to dope GaN, the highest available free hole concentration can reach the low 18th order due to the high ionization energy of Mg in GaN (0.2–0.15 eV for the Mg concentration between 1 × 1018 and 5 × 1019 cm−3) [1]. Such a hole concentration has enabled high-efficiency blue LEDs. However, the even higher ionization energy of Mg in AlGaN leads to a much lower hole concentration than the 18th order in p-type AlGaN. The ineffective p-type doping in AlGaN has severely hindered the development of AlGaN-based ultraviolet (UV) LEDs. A higher Al composition in AlGaN for shorter UV wavelengths would...
result in a higher ionization energy of Mg (e.g. \(\sim 0.5\) eV for AlN:Mg) [2–4]. At present, all AlGaN-based LEDs employ p-type GaN as their hole injector. The thickness of the p-type GaN is typically 100–200 nm thick as needed for a p-type contact layer. Due to the lattice mismatch between GaN and AlGaN, the quality p-type GaN is often degraded, which further decreases the hole concentration in p-type GaN. On the other hand, n-type nitrides can reach a fairly high electron concentration level (close to 19th order), leading to a severe imbalance between the electron and hole concentrations within the active region [5]. The insufficient hole supply for III-nitrides contributes to the poor performance of LEDs made therefrom.

To improve the free hole concentration in high-Al content AlGaN materials, researchers have developed the approach of polarization doping [6–10] for the purpose of enhancing electrical conductivity. By linearly grading the Al composition of AlGaN, the polarization bound charge spreads to a 3D form and induces the formation of a mobile 3D carrier gas of the opposite charge, resulting in an increased carrier concentration [11–15] over impurity doping. However, to produce substantial effective doping, there must be a strong composition gradient (a large range of Al:Ga ratio). This capability diminishes as the Al composition in AlGaN quantum wells approaches the binary endpoint, AlN, which is necessary to generate high energy photons. Another method to improve the hole concentration requires the use of nanowires [16] where high strain can be accommodated in p-type GaN such that an improved fraction of Mg ionization in GaN is expected. Nevertheless, all these methods are incremental measures to improve the free hole concentrations in the quantum wells of UV LEDs.

In this paper, we describe a novel measure to substantially increase the hole concentration in nitride-based multiple quantum wells (MQWs). Instead of using Mg-doped nitride as the hole supplier, we used p-type Si for nitride-based MQWs. Since Si can be heavily doped (20th–21st order) into p-type Si using boron atoms, for which the ionization energy of boron is in the level of thermal energy, even if partial (e.g. \(\sim 10\%\)) free holes in Si can be injected into the nitride-based MQWs, the imbalance between electron and hole concentrations in the MQWs could be greatly improved. However, the epitaxy of GaN on Si is challenging mainly due to a remarkable lattice mismatch. Si(111) plane is commonly chosen due to its trigonal symmetry facilitating a hexagonal Wurtzite structure. Due to lattice parameter differences, i.e. 0.3823 nm for Si (111) versus 0.3112 nm for AlN (0001) (or 0.3189 nm for GaN (0001)), the interface density of states can be very high with epitaxial growth [17]. The extensive practice of direct wafer bonding between two materials, which leads to poor interface quality with a very high density of interface states, has also proven to be infeasible for forming Si/GaN junctions of needed quality [18].

To solve the lattice mismatch challenge, we employed the ultrathin oxide interface heterostructure method [19, 20] to realize the Si/III-nitride isotype heterojunction. By inserting a layer of ultrathin oxide in between two semiconductors of any sized lattice constants, the two semiconductors are physically separated. As a result, interface defects due to lattice mismatch and/or crystal disorientation, as happens in wafer bonding, can be avoided. Without the concern of lattice mismatch, Si[100] was adopted based on the SOI material availability. The oxide type was selected such that it could effectively passivate the surfaces of the two semiconductors. If the oxide is sufficiently thin, it will serve as a quantum tunneling layer that allows the passage of both electrons and holes. The thickness of the oxide was determined by satisfying the requirements of both the surface passivation and efficient quantum tunneling. Practically, for a p–n diode fabricated using the heterostructure method, the influence of the oxide thickness is reflected on the diode ideality factor, rectification ratio, and reverse breakdown characteristics. With an optimum thickness of the oxide, ideal p–n diodes are readily achievable [20].

Since most oxides have plasticity at certain elevated temperatures, the oxides can serve as a thermal buffer layer that eases the bonding of the two semiconductors during chemical bonding to form the heterostructure.

The abovementioned heterostructure method is supposed to provide a universal scheme to form ideal abrupt junctions between dissimilar bulk (3D) semiconductors with minimum interface density of states. Nevertheless, application of the unique lattice-mismatched heterostructure method to solve the poor p-type doping challenges of III-nitrides has been very limited [21].

In this study, we formed a p-type Si/p-type GaN junction to enable the p-type Si as a hole injector. Heavily p-type doped Si nanomembrane (NM) was released from silicon-on-insulator (SOI), transferred and chemically bonded via rapid thermal anneal (RTA) to a p-type GaN layer that was first coated with a 0.5 nm thick Al\(_2\)O\(_3\) layer using atomic layer deposition (ALD). Al\(_2\)O\(_3\) is already well-known to be able to passivate both Si [22, 23] and GaN [24, 25] effectively. The 0.5 nm thickness of the ALD Al\(_2\)O\(_3\) layer was decided based on the best measured current density–voltage characteristics of p-Si/Al\(_2\)O\(_3\)/p-GaN heterostructures. High-resolution transmission electron microscopy (HRTEM) was used to reveal the detailed lattice structure of the Si/Al\(_2\)O\(_3\)/GaN interface. The electrical conductivity and band alignment of the p-type Si/GaN isotype junction were experimentally examined via current–voltage (\(I–V\)) and capacitance–voltage (\(C–V\)) characterizations. The calculated band alignment information was then used to examine the hole injection condition into AlGaN/AIN MQWs via simulations. Finally, UVC LEDs sequentially consisting of 100 nm transferred p-type Si, 0.5 nm ALD Al\(_2\)O\(_3\), and an epitaxially grown structure including 20 nm p-GaN, 2 nm Al\(_{0.75}\)Ga\(_{0.25}\)N/ 6 nm AlN x 3 MQWs,
and 600 nm n-type Al$_{0.74}$Ga$_{0.26}$N on an AlN substrate were demonstrated with high performance to prove the practicality of using p-type Si as an efficient hole supplier.

2. Results and discussion

2.1. Si/GaN heterojunction formation

Figure 1 illustrates the Al$_2$O$_3$-interfaced Si/GaN junction formation method and fabrication process flow. In brief, a 0.5 nm thick Al$_2$O$_3$ layer was deposited using ALD on a 200 nm thick p-type GaN layer that was grown on an MQWs LED epitaxial structure. A heavily boron doped ($5 \times 10^{19}$ cm$^{-3}$) SOI substrate was used to create single-crystalline Si NM of 100 nm thick by sacrificially etching away the buried oxide using hydrofluoric acid. The released p-type Si NM was transferred to the Al$_2$O$_3$-coated GaN using the PDMS stamp and a thermal anneal was applied to form chemical bonding. Metal electrodes were formed on the Si and GaN surface via photolithography.

Figure 1. Formation of Al$_2$O$_3$-interfaced Si/GaN junction. (a) Schematic illustration of the fabrication process flow. (i)–(ii). A heavily boron doped (5 × 10$^{19}$ cm$^{-3}$) SOI substrate was used to create single-crystalline Si NM of 100 nm thick by sacrificially etching away the buried oxide using hydrofluoric acid. (iii) Pick up the released Si NM using a polydimethylsiloxane (PDMS) stamp. (iv)–(v) A 0.5 nm thick Al$_2$O$_3$ layer was deposited using ALD on a 200 nm thick p-type GaN layer that was grown on an MQWs LED epitaxial structure. (vi) The Si NM was transferred to the Al$_2$O$_3$-coated GaN using the PDMS stamp and a thermal anneal was applied to form chemical bonding. (vii) Metal electrodes were formed on the Si and GaN surface via photolithography. (b) A 3D illustration of the metalized p-Si/Al$_2$O$_3$/p-GaN heterojunction.
to the larger lateral current spreading resistance in the p-GaN region. Furthermore, the C–V measurements of the p-Si/Al₂O₃/p-GaN heterojunction were carried out at a sweeping frequency of 1 MHz. The flat-band voltage was extracted to be −0.97 V from the 1/C²–V plot (figure 2(c)), which indicated a built-in potential Φ of −0.97 eV for the p-Si/Al₂O₃/p-GaN heterojunction. Since the free hole concentration of p-Si (5 × 10¹⁹ cm⁻³) is more than one order of magnitude higher than that of p-GaN (∼1 × 10¹⁸ cm⁻³), it is reasonable to assume that the built-in potential mainly originated from the p-GaN (one-sided junction), which was manifested as a 0.97 eV downward band bending of the Ga-polar surface in the p-GaN, as shown in figure 2(d). Additionally, x-ray photoelectron spectroscopy (XPS) was employed to examine the surface/interface of p-GaN with Al₂O₃ ALD deposition (figure A1 in the supplementary information (SI) is available online at stacks.iop.org/NJP/21/023011/mmedia), which revealed a downward band bending value of 1.00 eV, consistent with the 0.97 eV band bending value obtained from the C–V analysis.

Based on the measurements of the built-in potential, the valence band offset between p-Si and p-GaN can be determined by the following expression [26]:

\[
\Phi = \Delta E_v = \delta_{p-Si} + \delta_{p-GaN}
\]

(1)

where Φ is the built-in potential, extracted as −0.97 eV. The energy differences, \(\delta_{p-Si}\) and \(\delta_{p-GaN}\), between Fermi levels and valence bands (\(E_F-E_v\)) for heavily doped p-Si and p-GaN (assuming an acceptor ionization ratio of 10% and no strain in GaN) were calculated to be −0.002 eV and 0.12 eV, respectively. Therefore, the valence band offset \(|\Delta E_v|\) is 1.092 eV for the p-Si/Al₂O₃/p-GaN heterojunction. In comparison to the intrinsic \(|\Delta E_v|\) value of 2.32 eV, which can be obtained directly from the electron affinity rule, the energy barrier for hole transport from p-Si to p-GaN was substantially lowered. It is noted that the 20 nm GaN layer should have some strain due to the lattice mismatch between GaN and AlGaN and the strain in GaN (the value is unknown) can change the bandgap of GaN and the band offset values. However, even if a fully strained GaN is considered, the valence band offset value change (estimated to be −~0.09 eV) is still too small to undermine the hole injection mechanism. As a result, a much larger concentration of holes can be injected from Si into the MQWs. This difference in energy barrier stems from the negative polarization charges on the surface of the Ga-face GaN, as well as a voltage drop across the interfacial layer induced by the polarization charge. It is also noted that it is the use of the 0.5 nm Al₂O₃ interfacial layer, which served as an effective passivation layer for both Si and GaN, that caused the reduced band downward bending of Ga-face GaN (figure A1(c) in the SI), and thus the reduced barrier height for hole transport. Based on the above analyses of the surface band bending and interface-induced valence band offset shift, the band alignment of the p-Si/Al₂O₃/p-GaN isotype heterojunction under equilibrium is depicted in figure 2(d). Under forward and reverse bias, the band diagrams are shown in figures 2(e) and (f), respectively. As can be seen, under forward and reverse directions of bias, holes are able to
transport across the heterojunction via intra-band tunneling and thermal emission, respectively, leading to quasi-Ohmic $I-V$ characteristics, as supported by the electrical measurements (figure 2(b)).

**2.3. Effects of p-Si/Al$_2$O$_3$/p-GaN heterojunction on hole injection in UVC LEDs**

To examine the effects of p-Si/Al$_2$O$_3$/p-GaN heterojunction on hole injection in UVC LEDs, two LED structures, shown in figure 3(a), were simulated using Silvaco®. Intra-band tunneling model was employed, and a polarization strength factor (a constant scale factor multiplied by the calculated spontaneous and piezoelectric polarization charges) of 0.4 was used in the simulations. There can be different types of screening effects to the field induced by polarization charge, which makes the scale factor smaller than 1 in most cases, such as ionization of dopant [27, 28]. The only difference between the two LED structures is their p-type sides: LED A has the p-Si/Al$_2$O$_3$/p-GaN heterojunction and the thickness of the p-type GaN layer is 20 nm, while LED B only has a 100 nm thick p-type GaN layer. After applying the band alignment of p-Si/Al$_2$O$_3$/p-GaN heterojunction as shown in figure 2(d), the band structures of LED A under zero bias (equilibrium) is plotted in figure 3(b)(i).

For comparison, the band structure of LED B is plotted in figure 3(b)(ii). Figure 3(c) plots the band structures of the two LEDs under forward bias. As can be seen from figure 3(c)(i), the 20 nm p-type GaN in LED A is fully depleted and becomes a drift region for holes under forward bias. The strong internal electric field in the p-GaN layer, which caused the steep bending, is a combined effect of polarization and applied voltage. As a result, the 20 nm p-type GaN does not function as a hole injector in LED A, but rather a hole transport layer. In contrast, the 100 nm p-type GaN in LED B is only partially depleted and therefore is a hole supplier layer (figure 3(c)(ii)).

For LED A, under forward bias, the hole transport from the p-type Si into the p-type GaN became easier, as the triangular-shape energy barrier between the p-type Si and p-type GaN (0.97 eV) became narrower (∼1 nm) than its equilibrium state (figure 3(b)(i)), as shown in figure 3(c)(i), to facilitate hole tunneling. The favorable overall energy band alignment enabled efficient hole transport from the p-type Si to the drift region, and further to the MQWs region.

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**Figure 3.** Electrical simulations of UVC LEDs examining the effects of p-Si/Al$_2$O$_3$/p-GaN heterojunction on hole injection. (a) Schematic illustration of two simulated LED structures. The two LED structures are identical, except that LED A consists of 100 nm p-Si, 0.5 nm Al$_2$O$_3$, and 20 nm p-GaN, and LED B only consists of 100 nm p-type GaN on their p-sides. (b) The band diagrams of (i) LED A and (ii) LED B under thermal equilibrium. (c) Band diagrams of (i) LED A and (ii) LED B under forward bias (driving current density: 100 A cm$^{-2}$). (d) Electron (red) and hole concentration (blue) distributions within the three QWs under forward bias for (i) LED A and (ii) LED B. In LED A, both the blue and green lines represent hole concentrations in the three QWs. The blue and green lines were obtained under hole concentrations of $5 \times 10^{19}$ cm$^{-3}$ and $1 \times 10^{20}$ cm$^{-3}$ in p-type Si, respectively. (e) Comparison of hole concentrations between LED A and LED B. LED A has much higher hole concentrations than LED B in the three QWs. The inset shows the plot in its logarithmic scale.
The ample hole supply from the p-type Si and the efficient hole transport path led to a much higher hole density in the MQWs of LED A than in LED B and thus a more balanced electron/hole density in LED A (the blue line in figure 3(d)(i)) than LED B (figure 3(d)(ii)), even though the p-type Si was only doped to the level of $5 \times 10^{19} \text{cm}^{-3}$. As the doping concentration of the p-type Si was increased to $1 \times 10^{20} \text{cm}^{-3}$ (without changing any other LED parameters), the hole density in the MQWs of LED A further increased (the green line in figure 3(d)(i)). The increase in hole density in the MQWs following the increase in the hole concentration in the p-type Si furthermore verified that the p-type Si functioned as a hole supplier.

Figure 3(e) plots the direct comparison of hole densities between the two LEDs in linear scale with the inset showing a logarithmic scale plot. It is observed that the hole density in LED A, especially within the first two QWs, is significantly enhanced in comparison to LED B. The enhanced density of holes in the MQW is expected to enhance the electron–hole radiative recombination and therefore, the performance of UVC LEDs. The more holes that are present in the MQWs, the higher the recombination rate. Figure B1 shows the higher recombination rate when the hole concentration in the p-type Si is higher. It is noted that the p-type Si hole injector approach used in this work is readily applicable to UV LEDs covering a broad range of wavelengths.

### 2.4. Experimental application of p-type Si hole injector to UVC LEDs

The epitaxial layers of LED A (figure 3(a)) were grown on an AlN substrate by low pressure organometallic vapor phase epitaxy (LP-OMVPE) in a custom high-temperature reactor (see the SI for details of epitaxial growth). Two different LED samples have been grown that differ only by the thickness of the p-type GaN layer. The 20 nm Mg-doped p-type GaN layer here was grown, and also serves as a barrier layer to circumvent the rapid oxidation of the AlN surface (see figure C1 in the SI). The procedure to form the p-type Si hole injector via Si NM transfer and bonding is identical to that shown in figure 1. A detailed LED fabrication process flow is shown in figure D1 in the SI. The completed three-dimensional UVC LED structure is illustrated in figure 4(a). Figure 4(b) shows a scanning electron microscope (SEM) image of a piece of Si NM that was bonded to the epitaxial LED layer. Figure 4(c) shows an SEM image of a part of a fabricated UVC LED and the inset shows an optical image of a top view of the LED.

It is crucial to maintain strain-free bonding during the bonding process, since the strain in the Si NM can create unwanted band bending or even surface states at the interface. In figure 4(d), the x-ray diffraction (XRD) 2-theta-omega scan range from 30° to 80° at ~0.05° steps taken from the completed p-Si/Al2O3/p-GaN/i-AlN/i-Al0.75Ga0.25N/AlN MQWs/n-Al0.75Ga0.25N/AlN structure shows three peaks corresponding to the AlGaN (002) direction, Al2O3 (002), and Si (001) directions, respectively. FWHM values of
$0.075^\circ$ and $0.1^\circ$ from AlGaN and Si indicate that both the AlGaN epi-layer and transferred Si NM layer maintained good crystallinity during the transfer/bonding processes. The appearance of the weak $\text{Al}_2\text{O}_3$ peak at $42.1^\circ$ in the XRD spectrum (figure 4(d)) indicates the existence of crystalline $\text{Al}_2\text{O}_3$, which may be attributed to the re-crystallization of the ALD interfacial $\text{Al}_2\text{O}_3$ during the annealing process. The weak intensity and the wide FWHM is attributed to the small thickness and may also imply that the ALD deposited $\text{Al}_2\text{O}_3$ was only partially crystallized, which is consistent with the HRTEM image shown in figure 2(a). To evaluate the strain of the Si/AlN/AlGaN heterostructure, Raman spectroscopy was carried out using a Horiba LabRAM ARAMIS Raman confocal microscope equipped with a $50\times$ objective lens and a monochromator that has a $1000\text{ mm}$ focal length with an $f/8$ aperture. The spectrometer resolution is $0.045\text{ cm}^{-1}$ and the laser spot size is about $1\text{ \mu m}$. The power of the $532\text{ nm}$ green excitation line ($\text{lexc}$) is $18.5\text{ mW}$. As shown in figure 4(e), the Raman characteristic peak for Si nanomembrane [29] that is taken from the Si/AlN/AlGaN heterostructure appeared at $237\text{ nm}$, (d) Measured light output power and the corresponding voltage applied to the LED versus current density applied. The dotted line was drawn to show the linear trend of the light output power.

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The measured current density–voltage ($J$–$V$) plot for the UVC LED (figure 5(a)) shows its rectifying characteristics. Figure 5(b) shows an optical image of an LED under forward bias with weak blue emission, most likely from the p-type GaN and deep levels elsewhere in the device, which is commonly reported in UVC LED literature [32, 33]. The linear scale of the electroluminescence (EL) spectra for various current densities from $15.3$ to $244.5\text{ A cm}^{-2}$ are depicted in figure 5(c), where the dominant emission peak appeared at $237\text{ nm}$, which is from the Al$_{0.72}$Ga$_{0.28}$N/AlN MQWs. With the current densities ranging from $15.3$ to $244.5\text{ A cm}^{-2}$, the intensity of the $237\text{ nm}$ emission peak monotonically increases with increasing drive. Alongside the main peak emission, there is another rather weak parasitic peak detected in the near-UV range. The parasitic peak, likely from excitation by $237\text{ nm}$ photons of the top p-type GaN combined with deep levels in AlGaN, is much weaker than that of the recently reported $232\text{ nm}$ UVC LED [7]. The measured light output power and applied voltage

Figure 5. Measured electrical characteristics and electroluminescence performance of a UVC LED. (a) Measured current density–voltage characteristics of the fabricated UV LED. (b) An optical microscope image of the UV LED under bias with weak blue electroluminescence. (c) EL spectra (linear scale) taken at drive currents ranging from 20 to $320\text{ mA}$. The main peak wavelength is $237\text{ nm}$. (d) Measured light output power and the corresponding voltage applied to the LED versus current density applied. The dotted line was drawn to show the linear trend of the light output power.
versus the current density \((L-I-V)\) of the LED is plotted in figure 5(d). It can be seen that the light output power increases linearly with current density up to 245 A cm\(^{-2}\), which is equivalent to a current of 320 mA. This linear behavior implies an absence of efficiency droop in this range, which directly results from the use of p-type Si as the hole injector. The fairly balanced electron–hole density improves quantum efficiency in comparison to the conventional p-type GaN-based hole injectors \([34]\). Besides the efficiency droop-free behavior, 265 \(\mu\)W output power was measured from the UVC LED at a current density of 245 A cm\(^{-2}\) with an external voltage bias of 27.3 V, corresponding to an external quantum efficiency of 0.016\% and a wall-plug efficiency of 0.003\%. The efficiency is presently limited by the use of the relatively thick 20 nm p-type GaN layer, which absorbs UVC light, and thick AlN layer (28 nm), both inducing unnecessary series resistance. The relatively large turn-on voltage is a result of the large resistance of the near intrinsic AlN electron blocking layer and the non-ohmic metal contact made on the n-type \(\text{Al}_{0.74}\text{Ga}_{0.26}\text{N}\) layer. Further optimizations of the LED structures are expected to lead to better performances. While this is not the highest reported efficiency \([33, 35]\), the results clearly indicate the advantages of using p-type Si as a hole injector given that our LED provides the high UVC output power under constant current mode, which includes self-heating effects. It is further noticed that the ultrathin oxide interfaced lattice-mismatched heterojunction approach is applicable to other combinations of materials for various applications \([20]\).

3. Conclusion

In summary, using transferred p-type Si as the hole injector via the ultrathin oxide-interfaced large lattice-mismatched heterojunction approach proves to be a viable route toward overcoming the poor hole injection challenge of deep-UV LEDs. The wide applicability of the approach could enable many new III-nitride-based junction devices. Applying the approach to LEDs of shorter wavelengths and large LED arrays may be one of the directions of future research.

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Competing interests

The authors declare no competing financial interests.

Author contributions

SJC, DL, and J-HS contributed to the work equally. All performed the research. DL, BM, RD, JDA, SJC, KK, ZM, WZ, and J-HS interpreted the data and wrote the manuscript. DZ contributed to manuscript writing; JDA managed research progress. ZM designed the research.

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References


[35] Hirayama H, Noguchi N, Yatabe T and Kamata N 2008 227 nm AlGaN light-emitting diode with 0.15 mW output power realized using a thin quantum well and AlN buffer with reduced threading dislocation density Appl. Phys. Express 1 051101
Supplementary Information (SI)

P-type silicon as hole supplier for nitride-based UVC LEDs

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Appendix A.: XPS measurements on p-GaN surface to determine band bending before and after Al$_2$O$_3$ ALD deposition

It was reported that a Fermi level pinning state existed at 0.4 eV to 0.8 eV below the conduction band of GaN with n-type doping, due to nitrogen vacancy or gallium-dangling bond [1]. To further investigate the origin of the p-GaN surface band bending, X-ray photoelectron spectroscopy (XPS) was employed to examine the surface/interface of p-GaN before and after Al$_2$O$_3$ ALD deposition. The core level energies of Ga 3d, N 1s, Al 2p, and C 1s and valence band maximum (VBM) of p-GaN were measured with respect to the Fermi level at the surface. XPS measures the binding energy of photoelectrons emitted from the surface of the material by the incident X-ray source with respect to the binding energy at the Fermi level ($E_F$). The energy scale 'eV' was chosen to represent the band bending of GaN by the shift of binding energy of atomic levels. Figure A1(a) represents the shift of atomic energy level in the bandgap energy of GaN and Figure A1(b) shows the energy difference between the Fermi level and VBM in the bandgap energy of GaN. The measurement results are shown in Figure A1. Ten times-repeated scans using Al K$_\alpha$ X-ray source ($h\nu = 1486.60$ eV) were performed with 0.1 eV scan steps, 100 µm spot size, 50 eV pass energy, and 50 ms dwell time. The binding energies of the Ga 3d peak before and after Al$_2$O$_3$ deposition were 19.36 and 19.03 eV, respectively, as shown in Figure A1(a). Thus, a 0.33 eV surface potential shift was measured on the p-GaN surface by deposition of Al$_2$O$_3$, with respect to the as-grown p-GaN surface. Furthermore, Figure A1(b) shows that the valence band maximum (VBM) of p-GaN is positioned at 1.45 eV below the Fermi level. Based on the above XPS measurement results, the band bending diagrams of p-GaN near the surface are depicted for the two scenarios (with and without Al$_2$O$_3$). Inferring from the 1.45 eV VBM in Figure A1(b) and $0.12$ eV $E_F - E_v$, the energy bands were downward bending about -1.33 eV (Figure A1(c) left) and -1.00 eV before and after (Figure A1(c) right) the Al$_2$O$_3$ deposition, respectively. It is worth pointing out that the XPS analysis matches the band bending results obtained from C-V measurements (Figure 2(c) in the main text), which reveals -0.97 eV downward bending of the p-GaN.
Figure A1. XPS measurements on p-GaN surface band bending before and after Al₂O₃ deposition.
(a) Binding energies of the Ga 3d peak before and after Al₂O₃ deposition. (b) VBM of p-GaN without Al₂O₃. (c) Energy bands before (left) and after (right) Al₂O₃ deposition.

Appendix B.: Epitaxial growth and p-type hole injector formation

LED A was grown using low pressure organometallic vapor phase epitaxy (LP-OMVPE) in a custom high-temperature reactor. The Al, Ga, N, Si, and Mg precursors were trimethylaluminum, triethylgallium, ammonia, silane, and bis(cyclopentadienyl)-magnesium, respectively, in a hydrogen diluent. The dislocation density of the AlN substrate is specified as 10⁴/cm² at its maximum and the misorientation of the wafers used for this work is 0.15°. As shown in Figure 3(a), following an initial 400 nm AlN homoepitaxial layer, the epitaxial portion of the active device is comprised of a Si (1x10¹⁹/cm³) doped 600 nm n-Al₀.₇₄Ga₀.₂₆N electron injection layer, a 3-period 2 nm Al₀.₇₂Ga₀.₂₈N/6 nm AlN MQW, and a 28 nm AlN electron blocking layer (EBL). A 20 nm p-type GaN was finally grown as a termination layer to protect the surface from oxidation in air.

On top of the epitaxial layer, i.e., p-type GaN, a 0.5 nm Al₂O₃ layer was deposited by atomic layer deposition (ALD) after cleaning by the standard RCA method. The 0.5 nm Al₂O₃ layer acted as a quantum tunnel layer and a passivation layer to form the needed lattice-mismatched heterojunctions [2]. A p-type
doped \((5 \times 10^{19} \text{ cm}^{-3})\) single-crystalline Si NM, which was pre-released from a silicon-on-insulator (SOI) substrate, was then transferred ((Figure 1(a)(iii) and (vi)) in the main text [3, 4] to the top of the \(\text{Al}_2\text{O}_3\) layer, followed by a rapid thermal anneal (RTA) procedure at 500°C for 5 minutes. The RTA procedure is intended to activate the chemical bonding process and increase the bonding strength between the p-Si NM and \(\text{Al}_2\text{O}_3\).

To directly correlate the hole concentration in the p-type Si and the electron-hole recombination and therefore the performance of UVC LEDs, simulations on the recombination rate comparison for LED A between two different hole concentrations in the p-type Si were carried out. The blue line denotes the recombination rate within the quantum wells for hole concentration of \(5 \times 10^{19}/\text{cm}^3\) in Si, and the green line is for the case of \(1 \times 10^{20}/\text{cm}^3\). As shown in Figure B1, as the hole concentration in Si increases two-folded, the recombination rate within the rightmost well (most dominant one among the three quantum wells) increases by the same amount. Thus, the function of the added Si layer as a hole injector layer is further verified, as a higher recombination rate is induced with an enhanced density of holes in the Si layer.

Figure B1. LED A Recombination rate comparison between two hole concentrations in the p-type Si. Blue line: \(5 \times 10^{19}/\text{cm}^3\). Green line: \(1 \times 10^{20}/\text{cm}^3\).
Appendix C.: AlN Native Oxide

Aluminum (Al) compounds are reactive and oxidize readily since Al has a strong affinity for oxygen [5, 6]. In addition, hydroxylation occurs when aluminum reacts with water vapor in the air. Thus, there exists an amorphous layer of a few nanometers thickness of one or several aluminum–oxygen–hydrogen compounds, such as aluminum trihydroxide (Al(OH)₃), aluminum oxide hydroxide (AlOOH or Al₂O₃·H₂O), or aluminum oxide (Al₂O₃) [5]. It has been reported [5, 7] that the formation of native hydroxides on freshly cleaned nanocrystalline, thin film, and bulk AlN occurs rapidly at room temperature. The typical thickness of the aluminum hydroxide is 2-5 nm, as further diffusion of oxygen is inhibited by the stable passivating layer.

This oxidation phenomenon was observed in our work. Figure C1 shows a HRTEM image of the interface between Si and AlN/AlGaN MQW, where Si NM was bonded to a AlN/AlGaN MQW in air and the native oxide was already formed before bonding the Si NM. Amorphous aluminum–oxygen–hydrogen compounds of ~7 nm thick were formed due to the exposure of the AlN/AlGaN MQW to the ambient air. In contrast to the thin and orderly interface between the Si NM and GaN shown in Figure 2(a), this amorphous layer severely limited the hole carrier transport into the MQW region. As a result, the 20 nm GaN layer in LED A was grown on top of the MQW as a termination layer for the epitaxy growth, which prevented the oxidation of AlN.

The transmission electron microscopy (TEM) specimen was prepared using FIB milling (Zeiss Auriga Focused Ion Beam). The images in Figure 2(a) in the main text and Figure C1 were obtained from a Tecnai T-12 TEM along the [001] zone axis and 120 kV acceleration voltage at room temperature.

Figure C1. A TEM image showing native oxide between bonded Si NM and AlN/AlGaN MQWs.

The native oxide was formed due to exposure of the AlN/AlGaN to air. The growth of 20 nm thick GaN (shown in Fig. 3a) protected the surface from oxidation in air.
Appendix D.: LED Fabrication Process

Figure D1 illustrates the UVC LED fabrication process flow. The LED epitaxial samples were cleaned by the standard RCA method (Figure D1(a)(i)): sonication of the samples in acetone, isopropyl alcohol (IPA), and deionized (DI) water for 10 min to remove particles and dust from the surface, followed by immersion in piranha solution (a mixture of H₂SO₄:H₂O₂ (4:1)) to remove metals and organic contaminants. Then the samples were immersed in SC-1 solution (H₂O:H₂O₂:NH₄OH (5:1:1)) and SC-2 solution (H₂O:H₂O₂:HCl (5:1:1)) for 10 minutes per solution at room temperature to remove any remaining organic contaminants, heavy metals, and ionic contaminants. Finally, the native oxide on the wafer surface (p-GaN) was removed using diluted hydrogen fluoride (HF) (1:50 of HF:DI water) followed by a thorough rinse in deionized (DI) water before drying with a nitrogen gun.

An Al₂O₃ layer of 0.5 nm was deposited using an Ultratech/Cambridge Nanotech Savannah S100 ALD system, which was integrated with a nitrogen filled glove box. The sample was loaded in the chamber after removing native oxide with HF. It should be noted that all the processes after finishing the removal of the native oxide layer were carried out in a nitrogen environment. The chamber was pre-heated to 200°C and pumped down to vacuum (<0.1 mTorr) immediately after loading the sample. During the ALD process, trimethylaluminum (TMA) gas and water vapor were purged for 0.015 s every 5 s. Five cycles of the ALD process were performed to achieve the targeted 0.5 nm thick Al₂O₃ layer as depicted in Figure D1(a)(ii).

A p-type single-crystal Si nanomembrane (NM) with a doping concentration of 5×10¹⁹ cm⁻³ [8] was first released from a silicon-on-insulator (SOI) substrate and then print transferred [3, 4] to the AlN/AlGaN MQW structure (Fig. S4a iii and Fig. S4b) following procedures that we described elsewhere [8]. A thermal anneal procedure was performed at 500°C for 5 min to increase the bonding strength between the p-type Si NM and Al₂O₃ deposited epitaxial structure. Using photolithography image reversal photoresist (PR) AZ5214 for patterning, reactive ion etching (RIE) (PT790 RIE Plasma Etcher, CF₄: 45 sccm, O₂: 5 sccm, pressure: 40 mTorr, plasma power:100 W) to etch away the Si NM, and inductive coupled plasma (ICP) etcher (PT770ICP Metal Etcher, BCl₃/Cl₂/Ar: 18/10/5 sccm, pressure: 20 mTorr, plasma power: 50 W, inductor power: 500 W) to etch the p-GaN/AlN/i-AlN/AlGaN MQW, the n-type Al₀.₇₄Ga₀.₂₆N was exposed to form a mesa (Figure D1(a)(iv) and Figure D1(c)). A stack of cathode metals (Ti/Al/Ni/Au: 15/100/50/250 nm) was deposited using an e-beam evaporator and photolithography. The sample was annealed at 950°C for 30 s to improve the cathode contact resistance (Figure D1(a)(v) and Figure D1(d)). Another stack of anode metal (Ti/Au: 15/100 nm) was formed in the same way as the cathode metal on Si NM (Figure D1(a)(vi) and Figure D1(e)) but without using thermal anneal. The LEDs were isolated by subsequently etching away the Si NM (Figure D1(a)(vii)), GaN layer, AlN layer, and MQW layer n-Al₀.₇₄Ga₀.₂₆N layer until the AlN substrate was exposed (Figure D1(a)(viii) and Figure D1(f)).
Figure D1. Illustration of UVC LED fabrication process and images. (a) Fabrication process flow. i) Begin with epitaxial layers and RCA cleaning. ii) Deposit 0.5 nm thick Al₂O₃ via ALD. iii) Transfer and bond Si NM and thermal annealing. iv) n-type mesa etching to expose Al₀.₇₄Ga₀.₂₆N. v) Formation of cathode metal stack Ti/Al/Ni/Au of 15/100/50/250 nm on the Al₀.₇₄Ga₀.₂₆N layer. vi) Formation of anode metal stack Ti/Au of 15/100 nm on Si NM. vii) Etching away Si NM. viii) Etching away GaN/MQW/AlGaN to expose AlN substrate. Optical microscope images corresponding to the processing steps. (b): a iii); (c): iv); (d): v); (e): vi); and (f): a vii).

Appendix E.: Electroluminescence (EL) measurement

In this LED design, light was only emitted through the n-AlGaN and AlN substrate as all emissions in the opposite direction were fully absorbed by the p-GaN and p-Si. However, the AlN substrates have significant absorption in the UV spectral range [9]. As a result, the substrates were thinned to 20 µm to reduce absorption losses prior to dicing into chips for EL evaluation. Even after thinning, absorption loss was estimated to be greater than 50%. No special light extraction measures were used.

The maximum applied current density was limited by the Keithley 4200 Semiconductor Parameter Analyzer. EL spectra and optical power measurements were performed by coupling the UV LED emission (without using any light extraction fixture) into the 6-inch integrating sphere of a Gooch and Housego OL 770-LED calibrated spectroradiometer. Electrical power was supplied in constant current mode and the temperature was not controlled, so LEDs were allowed to self-heat.
Appendix F.: The optical loss estimation of the LEDs.

Si is known to be highly absorptive in the UV range due to its small bandgap. In our LED design, UV absorption in Si becomes less important as the light penetration depth in Si is extremely short. Instead, UV light was mostly reflected rather than absorbed at the Si surface for the following reason.

As shown in Figure F1, the UV reflectance (R) at 237 nm under a normal incidence at the interface between GaN and AlN \((n_{\text{AlN}} = 2.57)\) \([10]\) is only 1% based on the Fresnel equation. In contrast, the reflectance of the same wavelength of UV light between Si \((n_{\text{Si}} = 1.59 + 3.35i)\) and GaN \((n_{\text{GaN}} = 2.71 + 0.57i)\) is 49%. A transmission coefficient of 54.1% is calculated for 20 nm GaN based on an absorption coefficient of \(\alpha = 3.1 \times 10^5 \text{ cm}^{-1}\) at 237 nm. As a result, the optical loss is 23% and 13% for the 20 nm GaN layer and the top Si layer, respectively. Note that the simplified estimation only considered light emission under a normal incident direction with respect to the surface. The multiple reflection-induced resonance effect within each layer was also assumed to be negligible.

![Figure F1. The optical loss estimation with the proposed p-Si/Al\(_2\)O\(_3\)/p-GaN/i-Al\(_2\)O\(_3\)/Al\(_0.72\)Ga\(_0.28\)N MQW/n-Al\(_0.74\)Ga\(_0.26\)N/AlN structure.](image)

Figure F1. The optical loss estimation with the proposed p-Si/Al\(_2\)O\(_3\)/p-GaN/i-Al\(_2\)O\(_3\)/Al\(_0.72\)Ga\(_0.28\)N MQW/n-Al\(_0.74\)Ga\(_0.26\)N/AlN structure.

Appendix G.: Potential contributors to the turn-on voltage.

The turn-on voltage of 16 V in our LEDs is about 10 V higher than the ideal turn-on voltage determined by the bandgap energy. We attribute the extra voltage drop to the following factors: 1) Tunneling junction voltage drop. For the p-Si/p-GaN junction there is about 1 V voltage drop before the current flow becomes ohmic-like. 2) Resistance-induced voltage drop in the 28 nm intrinsic AlN. 3) The non-ohmic metal contact with the n-Al\(_{0.74}\)Ga\(_{0.26}\)N layer. For the metal contact, due to the high Al composition, the metal contact on Al\(_{0.74}\)Ga\(_{0.26}\)N shows Schottky behavior rather than Ohmic, which contributes to about 4 V turn-on voltage.

Regarding each of the above factors, approaches to reduce the turn-on voltage include: 1) heavy doping Si and GaN to further reduce the depletion width and increase the tunneling probability; 2) adopting a graded p region by increasing Al composition from p-GaN to AlN gradually; and 3) optimizing the metal contact on AlGaN, such as adjusting the annealing temperature or attempting different metal schemes.
Supplementary References


