AlGaN nanowires with inverse taper for flexible DUV emitters

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Abstract
Deep ultraviolet (DUV) AlGaN light-emitting diodes (LEDs) are promising alternatives for production of DUV light, offering many advantages over mercury arc lamps. In this work, AlGaN nanowires with an inverse taper profile were demonstrated through a wet etching process, enabling removal of the nanowires from the growth substrate in a novel peeling process to form flexible devices. AlGaN nanowires with taper angles of ~22° were obtained following a 70 min etch in AZ400K. Nanowire taper angle was studied as a function of etch time and nanowire top diameter. Released nanowires embedded within the polymer liftoff layer exhibit strain relaxation induced redshift due to reduction in piezoelectric polarization electric field intensity. The inverse taper structure was found to promote enhanced light extraction from the nanowire. The demonstrated flexible DUV emitters with inverse taper are shown to improve the device efficiency and allow for realization of flexible emitters through a novel fabrication process for the first time.

1. Introduction

AlGaN deep ultraviolet (DUV) light-emitting diodes (LEDs) show promise for use in applications such as water purification, pathogen neutralization, and medical treatments [1–4]. In contrast to mercury vapor arc lamps, DUV LEDs offer a small form factor, tunable emission wavelength, long lifetime, and environmental compatibility [1, 5]. DUV LEDs are usually fabricated as planar mesa devices due to the maturity of the fabrication process. Nanowire DUV LEDs, while more difficult to fabricate, offer higher light extraction efficiency (LEE) and improved internal quantum efficiency (IQE), which together produce significant enhancements in external quantum efficiency [6]. Nanowire LEDs can be formed through a bottom up growth approach, which allows for large reductions in defect density through use of specialized growth substrates, further enhancing their IQEs when compared to planar LEDs [7]. Though nanowire LEDs have a number of beneficial properties, a reliable process to remove them from the growth substrate has not yet been developed, as it has for planar LEDs [8]. LEDs removed from the growth substrate offer new possibilities for flexible electronics and photonics, and enable reuse of the epitaxial substrate. Previous work on flexible nanowire LEDs typically involves embedding the nanowires in a flexible polymer for support, followed by mechanical exfoliation with a razor blade [9]. As a requirement for this process, the nanowires must be grown to at least 20 µm tall, and even then, the approach still suffers yield issues [10]. Therefore, a more reliable and stable process is needed to realize flexible DUV LEDs.

Our previous work demonstrated that hydroxyl-based chemistries can wet etch GaN and remove dry etch induced damage, as the OH− ions in these solutions exhibit a unique crystallographic etching in wurtzite GaN and AlInGaN alloys [11]. Hydroxyl based chemistries also allow for formation of vertical GaN nanostructures with perfectly smooth sidewalls [11]. These chemistries do not etch Ga-polar surfaces, such as the c-plane (0001) of wurtzite GaN and AlInGaN alloys, instead rapidly etching the semi-polar r-planes (1011) until the non-polar (1010) plane is revealed, which is then etched more slowly [12]. This unique
crystallographic etch rate variation is due to differences in both the surface polarity as well as the surface energy/dangling bond density of the surface. Surfaces which develop higher densities of electronegative dangling bonds (such as the $c$-plane), will repel hydroxyl ions in solution, preventing them from accessing the surface and lowering the etch rate \[11–13\]. This phenomenon can be applied to transform a flared cone into a nanowire. Typically, a cone-like taper is formed through a dry-etch which can be transformed into a vertical hexagon with vertical sides, without reducing its height. However, this process is not well studied for UV and DUV LEDs, and existing research has not yet applied this wet etching process to high Al-content AlGaN nanowire structures for extended etch times \[13\]. Here, high Al-content AlGaN nanowires are etched in a hydroxyl-based solution for up to 70 min. Etch rates and sidewall angle dependence on etch time are investigated in order to better understand the physical mechanisms responsible for formation of the inverse taper profile which we have observed for the first time in high Al-content AlGaN nanowires. With this novel method of forming AlGaN nanowires with an inverse taper, a flexible DUV LED is achieved in this study using a polymer liftoff process, which allows for reliable, high yield release of the nanowires from the substrate.

2. Experimental setup

In this work, an AlGaN epitaxial stack emitting at 267 nm grown using metal organic chemical vapor deposition on a sapphire substrate with a Ga-polar $c$-plane orientation was used as the basis for the nanowire LED. The epitaxial stack consisted of 1 $\mu$m of AlN grown on a sapphire substrate, followed by 2 $\mu$m of $n$-Al$_{0.55}$Ga$_{0.45}$N, a 75 nm AlGaN multiple quantum well, a 20 nm $p$-Al$_{0.60}$Ga$_{0.40}$N electron blocking layer, 40 nm of $p$-Al$_{0.55}$Ga$_{0.45}$N, and 160 nm $p$-GaN. This epi stack is shown in figure 1(a). The nanowire dry etch hard mask consisted of 200 nm thick Ni dots patterned with laser direct-write lithography with diameters ranging between 1 and 2 $\mu$m (figure 1(b)). A Plasma-Therm Apex inductively coupled plasma (ICP) etcher was used to perform the dry etch, forming AlGaN nanowires with a 'normal' taper in which the base diameter is larger than the top diameter, as shown in figure 1(c). The gas flow rates for the dry etch were 40 standard cubic centimeters per minute (sccm) of Cl$_2$ and 10 sccm of Ar at a chamber pressure of 30 mtorr. An ICP plasma power of 500 W and a forward power of 225 W were used to produce the desired nanowire geometry. De-ionized (DI) water with 40% AZ400K photoresist developer (2% KOH by weight) at 80 $^\circ$C was chosen based on previous work, which shows that this solution leads to smooth, vertical sidewalls in GaN LED nanostructures \[11\]. The wet etch was performed in steps, with scanning electron microscope (SEM) images taken after each etch step, in order to study the effects of etch.

3. Fabrication of AlGaN nanowire with inverse taper and discussions

The DUV wafer was first subjected to a solvent clean consisting of a 5 min immersion in acetone followed by a 5 min immersion in isopropyl alcohol, and a 5 min rinse in DI water. The wafer was then coated with lift-off resist and photoresist and patterned with 1–2 $\mu$m openings using laser direct write lithography. Ni was deposited with a thickness of $\sim$200 nm and lifted-off, forming the Ni dots of the dry etch hard mask. Following the hard mask patterning, nanowires with heights of $\sim$2.2 $\mu$m were created with a Cl-plasma ICP dry etch. The initial nanowire etch profile produced by the ICP dry etch was cone-like, with the base of the nanowire having a larger diameter than the top. To study the effects of the AZ400K etching on the nanowires, 40% AZ400K in DI water at 80 $^\circ$C was chosen based on previous work, which shows that this solution leads to smooth, vertical sidewalls in GaN LED nanostructures \[11\]. The wet etch was performed in steps, with scanning electron microscope (SEM) images taken after each etch step, in order to study the effects of etch.
time on the morphology of AlGaN nanowires (figure 2). The sample was etched in 40% AZ400K solution for a total of 70 min with SEM images taken at 5, 10, 20, 30, 50, and 70 min shown in figure 2. In stark contrast to work with visible nanowire LEDs [11], the AlGaN nanowires show a distinct undercut which increases with etch time, rather than maintaining a vertical sidewall profile independent of etch time. This undercut phenomenon was observed for multiple different samples with high Al-content. The etch is overtly crystallographic as evidenced by formation of a hexagonal axial cross section for all wires, but the selectivity of the wet etch against the various wurtzite crystal planes appears different for this high Al-content material. As with hydroxyl-based etching of GaN, the Ga-polar $c$-plane is unaffected by the etch. The nanowires do not decrease in height as the etch progresses, and in instances where the Ni hard mask has delaminated, the tops of the wires are not attacked by the etch chemistry. The Ga polar surface of the $c$-plane repels the hydroxyl groups, resulting in a negligibly slow etch rate, while the non-polar planes [1011] are readily etched. The height, base, and top dimensions of the nanowires are used to calculate the undercut angle $\theta$. While the height and top diameter remain constant, the base diameter shrinks as the etch progresses. Figure 3 displays the undercut angle $\theta$ as a function of etch time. The undercut angle shows a semi-linear relationship with etch time, with an undercut angle of $\sim 22^\circ$ realized after 70 min in the etch solution. Undercut angle $\theta$ was found to be independent of wire diameter for nanowires of the same height.

It is also found that if an AlGaN nanowire is etched long enough, the diameter of the base will approach zero, causing the nanowire to detach from the substrate and fall over. As $\theta$ is independent of nanowire top diameter and increases at the same rate independent of nanowire diameter, it is evident that nanowires with a smaller top diameter will detach from the substrate sooner than those with larger top diameters. For example, figure 4(a) shows nanowires with top diameters of 1.25 $\mu$m after 70 min in etch solution, while figure 4(b) shows nanowires with top diameters of 1 $\mu$m after 70 min in etch solution. The smaller nanowires in figure 4(b) have detached from the substrate, while those in figure 4(a) have not. Whether a nanowire will
Figure 4. (a) Nanowires with 1.25 µm top diameters following 70 min KOH etch; (b) nanowires with 1 µm top diameter following 70 min KOH etch.

Figure 5. (a) Wurtzite unit cell highlighting the (0001) c-plane surface, (b) wurtzite unit cell highlighting the (10\bar{1}0) m-plane and semi-polar planes attacked by the AZ400K etch.

detach from the substrate after an arbitrary time in the hydroxyl-based etch chemistry depends upon the top diameter and height of the nanowire, as these parameters in conjunction with the undercut angle determine the base diameter of the nanowire.

The undercut and resulting inverse taper profile are caused by the polarity-selective nature of the hydroxyl based etch, with Ga polar surfaces repelling the hydroxyl groups while the N-polar, semi-polar, and non-polar planes are more easily etched. The relevant wurtzite crystal planes are shown in figure 5. The top surface of the nanowire is the Ga-polar (0001) plane (figure 5(a)), which remains unaffected by the etch, repelling the hydroxyl groups in the etch solution. The ICP dry etch is engineered to form nanostructures with relatively straight sidewalls which expose the non-polar (10\bar{1}0) plane. With conventional GaN LEDs an equal Ga:N ratio exists and a controlled etch peels back layers of this plane, following a cavity etch model and reducing the diameter while maintaining a vertical wire \[12\]. The cavity model of the progressing wet etch can be thought of as the inverse of growth \[13–16\]. Incorporation of the Al into the hexagonal crystal structure modifies the 1:1 Ga:N ratio, with Al atoms occupying Ga sites in the crystal lattice. The hydroxyl-based etch must therefore overcome a larger energy barrier in order to remove Al atoms from the surface due to the Al–N covalent bond having a stronger binding energy (11.5 eV/atom) than the Ga–N covalent bond (8.9 eV/atom) \[17\]. In the case of AlGaN DUV nanowires it appears the initial plane approximation of the (1010) is etched to the (20\bar{1}1) towards the (10\bar{1}1) plane \[16\]. This novel inverse taper structure can be exploited to aid in the removal of the nanowires from the underlying substrate.

4. Flexible nanowire emitter results and discussions

This nanowire morphology with inverse taper can be applied to aid in removal of nanowires from the substrate via a novel peeling process to enable flexible device applications. AlGaN nanowires with top diameters from 1.25 µm to 2 µm were subjected to a 70 min wet etch in 40% AZ400K at 80 °C to produce an undercut of \(\sim 22^\circ\). Reduction of the nanowire base diameter makes it easier to remove the wires from the substrate by reducing the cross-sectional area of the wire at the point at which it is mechanically separated.
from the substrate. In order to identify the prior location of the nanowires on the substrate following mechanical removal, a directional metal deposition is performed which leaves a circular ‘shadowed’ area beneath the tapered wires, as shown in figure 6. PDMS is used to remove the wires from the growth substrate due to its flexibility, chemical inertness, and high transparency in the DUV range. The PDMS is spin-coated onto the substrate to a thickness of 1 mm and acts as both mechanical supporting layer for the nanowires as well as a flexible host substrate following removal of the wires from the growth substrate, as shown in figure 6.

Following application of the PDMS, the sample is cured at 90 °C for 1 h to increase the nanowire-PDMS adhesion and improve the mechanical stability of the PDMS film. The sample is then submerged in 100% AZ400K at room temperature to release the embedded nanowires from the host substrate. The AZ400K will not attack the PDMS or the AlGaN substrate, but slowly works its way along the interface between them, delaminating the PDMS from the underlying AlGaN and further etching the bases of the nanowires. This process is very slow, and can take anywhere from hours to days depending on the size of the sample, as the etch chemistry must progressively delaminate the PDMS film in order to access the bases of all nanowires embedded in the film. The narrow bases of the wires are further etched until the wires are nearly or completely removed from the underlying AlGaN layer. Were the nanowires not embedded in PDMS they would tip over onto the substrate, as shown in figure 6(b). The PMDS acts as a mechanical support layer, maintaining the orientation and relative positions of the nanowires. After the AZ400K etch is complete, the PDMS film can be easily peeled from the original substrate as shown in figure 6(a). It can be seen that the nanowires are completely removed from the host substrate by this process, with the openings in the metal film the only indication of their prior locations, as shown in figure 6(b). The bases of the removed nanowires can be seen sticking through the bottom of the peeled PDMS film in figure 6(c). It is found that the nanowires from 1.25 µm to 2 µm are successfully removed from the host substrate. The peeled film exhibits exceptional flexibility despite containing thousands of rigid nanowires. Repeated flexing of the PDMS film does not appear to disturb the location and orientation of the embedded nanowires or damage the nanowires in any way. The AZ400K etching is found to be critically important for successful removal of the nanowires from the substrate. Without the extended AZ400K etch to delaminate the PDMS from the substrate and further reduce the base diameters of the nanowires, it is not possible to remove the nanowires using this
method. The mechanical shear force applied to the wires by peeling the PDMS film from the substrate is not sufficient to separate the wires from the substrate. This novel AZ400K etching and PDMS peeling process enables removal of very short nanowires from the substrate without the damage incurred by conventional mechanical exfoliation techniques. As the nanowires are fully removed from the substrate without leaving broken stubs, it is possible for the AlN growth substrate to be reused for epitaxial growth of additional LEDs.

Optical characterization of the nanowires was performed before and after removal from the substrate in order to examine the effects of the peeling process on the light emission properties of the nanowire emitters. A low-pressure mercury arc lamp emitting at 254 nm was utilized to collect the photoluminescence intensity. Figure 8(a) shows the emission spectra of the nanowires before and after the peeling process. Prior to removal from the substrate an emission peak was observed at 267 nm. After embedding the nanowires in PDMS and removing them from the substrate, the emission peak was observed to redshift by 25 nm from 267 nm to 292 nm. This distinct emission at 292 nm indicates that the nanowires are intact and that the PDMS film is transparent to DUV light. In addition to its flexibility and chemical inertness, PDMS exhibits a low absorption coefficient across the DUV emission range and an index of refraction of \( n = 1.46 \) which aids light extraction from the nanowires [18]. In addition to the 25 nm redshift, the nanowires show a significant increase in longer wavelength emission following removal from the substrate, which can be attributed to luminescence of defects in the PDMS film. The 25 nm red shift of the emission peak can be attributed to a reduction of the quantum confined stark effect (QCSE) [19]. Lattice mismatch induced strain causes powerful piezoelectric polarization electric fields to develop in the QW active region which raise the electron and hole ground states further from their respect band edges, shifting the emission wavelength of the primary exciton transition. Removal the nanowires from the substrate reduces this strain, reducing the internal electric fields in the QW and flattening the energy bands in the quantum wells, redshifting the emission spectrum by moving the electron and hole ground states closer to their respective band edges. Once the nanowires are removed from the substrate they can either be transferred to an alternative substrate (and the PDMS removed via dry etch) or remain embedded in the PDMS which can act as a virtual, flexible substrate, enabling development of flexible DUV LEDs.

We have also investigated the effects of this novel structure on the efficiencies of the individual nanowires composing the LED. Finite-difference time-domain (FDTD) studies were performed to determine the effect of the inverse taper structure on the LEE of the nanowires at DUV wavelengths. Nanowire structures are utilized to improve the extraction of transverse magnetic (TM) polarized light from DUV LEDs because TM-polarized emission dominates at shorter wavelengths due to valence band mixing effects in high Al-content AlGaN [20], so it is important to confirm that this novel inverse taper structure preserves or improves both TM and transverse electric (TE) polarized LEE. Note that while our nanowires emit at either 267 nm or 292 nm, where TE polarized emission is dominant, it is still important to study both TE and TM polarized LEE as the TM contribution to emission at these wavelengths is non-negligible. Figure 8(b) plots the LEE for an AlGaN nanowire with a height of 2.2 \( \mu m \) and a top diameter of 1 \( \mu m \) as a function of the sidewall angle \( \theta \) at an emission wavelength of 270 nm. It is evident that significant enhancements in LEE can...
be achieved through formation of a minimal inverse taper structure, with sidewall angles of $20^\circ$ increasing TM-polarized LEE to more than 90% compared to less than 50% for a sidewall angle of $0^\circ$. Also of note, ‘normally’ tapered nanowires whose base diameters are greater than their top diameters ($\theta < 0^\circ$) are shown to decrease LEE relative to nanowires with vertical sidewalls ($\theta = 0^\circ$) likely because these structures serve to deflect TM polarized photons down into the substrate. These results show that, in addition to enabling enhanced liftoff from the growth substrate, AlGaN nanowires with an inverse taper could also be utilized to produce significant enhancements in LEE, an area in which DUV LEDs are conventionally limited.

5. Conclusions

Our work presented a flexible DUV emitter based on high Al-content AlGaN nanowires with an inverse taper profile that enables their removal from the growth substrate. The time-dependent effects of a hydroxyl based crystallographic wet etch on the morphology of high Al-content AlGaN nanowires, specifically the undercut angle, was studied. Undercut angles of $\sim 22^\circ$ were obtained after 70 min in 40% AZ400K at 80 $^\circ$C. The formation of this undercut can eventually lead to complete removal of the nanowires from the underlying substrate as the etch progresses. This undercut enables a unique PDMS peeling process capable of removing the nanowires from the growth substrate while maintaining their orientations and relative positions. The AlGaN nanowires removed from the substrate and embedded in PDMS show a 25 nm red shift in peak emission wavelength from 267 nm to 292 nm due to a reduction of the QCSE through strain relaxation. FDTD simulations indicate that the nanowires with an inverse taper structure can enhance LEE from less than 50% to more than 90% when compared to nanowires with vertical sidewalls. Following further development, this novel nanowire peeling process could enable both unique high-efficiency flexible light emitting devices as well as high-yield nanowire transfer processes.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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