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14. ABSTRACT

A process is developed to transfer epitaxially grown III-nitride films onto substrates more applicable to the desired application. The substrates for epitaxial growth of these films are limited to single-crystal sapphire, gallium nitride (GaN)-on-sapphire templates, or free-standing GaN. However, the desired end application requires a different substrate for optical, electrical, or thermal reasons. This process is applied for a semipolar (20-21) GaN lasing stack, grown on free-standing GaN, and designed for emission at a wavelength of 369 nm. A sacrificial indium gallium nitride (InGaN) layer, with an emission wavelength of 410 nm, is grown below the lasing stack. The stack is processed into 200 mesa structures to minimize the amount of undercut etch-rate limitations. The etching is performed in a 0.1-M potassium hydroxide solution under backside irradiation from a 405-nm laser such that only the sacrificial layer absorbs the incident radiation. The photogenerated holes induce a surface oxidation current, etching the sacrificial InGaN layer and promoting the release of the epitaxial lasing stack, which can then be automatically transferred to a previously bonded heterogeneous substrate.

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1. Introduction

The III-nitride class of materials (aluminum nitride [AlN], gallium nitride [GaN], indium nitride, and corresponding ternary alloys) provide a basis for a variety of electronic and photonic devices across several different applications. Epitaxial growth techniques, such as molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), however, limit the growth of these materials on lattice-matched substrates. Due to the wurtzite hexagonal crystal structure of the III-nitrides, substrates on which these materials are grown have been mostly limited to aluminum oxide (Al_2O_3, single-crystal sapphire), a GaN-on-sapphire template, or free-standing GaN.

In some applications of grown III-nitride structures, the substrate can limit the performance or prevent successful operation. For example, applications that require an optically transparent substrate in the UV spectral region are either to perform optical experiments on the grown materials and/or in the application's final implementation or a substrate with high thermal conductance to mitigate localized heat generation due to high carrier densities. These reasons, among others, necessitate the use of a different substrate due to sapphire's low thermal conductivity and GaN's limited optical transparency window.

Specifically, the desired application is a GaN-based lasing stack with an emission wavelength of 369 nm and driven by an electron beam irradiation, which leads to high carrier densities. This necessitates the transfer/removal of the GaN substrate (or GaN-on-sapphire) to diamond, which has a high optical transparency and thermal conductivity. Therefore, a method has to be developed to enable the transfer of a GaN lasing stack onto a diamond submount. Although GaN liftoff from sapphire has been demonstrated with laser irradiation,[1] the physical principle is based on the absorption, heating, and dissociation of GaN at the GaN-sapphire interface, which causes some minimal surface damage that could negatively impact optical transmission of the emitted light. Since this work requires the isolation and transfer of a specific region, a more refined technique is required to transfer the grown material.

The method chosen to achieve substrate transfer is photoelectrochemical (PEC) etching, in which a region or a part of the material stack is selectively etched off in an electrolyte solution in response to photogenerated carriers from light absorption. Due to the photo-oxidation process at the surface of the release layer, corrosion occurs, and the release layer is dissolved in solution. PEC etching was first demonstrated for GaAs[2] and then GaN[3] to process wafers with a controlled material-removal technique. This process was then extended to creating surface

features on GaN patterned by cathodic metal deposition[4] and creating pillar/disk microstructures by etching buried InGaN layers within GaN.[5,6] The ability to change the bandgap of the material across the III-nitride alloy system allows for light-absorption selectivity within the PEC etch layer, hence the design to use InGaN etch layer around a GaN release stack. Recently, this technique has been refined with band engineering within the release layer[7] and extended to the point where it has been used to integrate metal-oxide distributed Bragg reflector mirrors on GaN-based vertical cavity surface emitting lasers.[8]

In this work, PEC etching is used as a processing step to enable transfer of a GaN-based materials stack lasing at 369 nm to a diamond submount.

2. Experiment

The materials are grown on free-standing semipolar (20-21) GaN substrates using MOCVD. First a 20-nm InGaN layer is grown as designed to have an In/Ga alloying fraction such that its emission wavelength is longer than the 405-nm laser source being used to initiate the etch. On top of the InGaN a 250-nm GaN layer is grown to serve as the layer that will be transferred through the PEC etch process.

After growth, the substrates are processed to enable liftoff. Mesas with a 200-μm diameter are lithographically defined and etched down to a depth of approximately 450 nm using a plasma etching chemistry of chlorine (Cl_2) and boron trichloride (BCl_3) gases. The etch depth is chosen to expose the InGaN PEC etch layer from the side of the mesa. Around the mesas, a cathode metal stack of titanium (Ti)/gold (Au) is deposited on the GaN surface. The purpose of the cathode metal stack is to source photogenerated electrons in the PEC release layer to complete the electrochemical reaction (both oxidation and reduction processes) to drive the etching. It is also important to have the cathode metal in close proximity to the etch layer such that the diffusion path for photogenerated electrons is minimized; otherwise, the reaction will either slow down or completely stop before the etch layer is completely dissolved. Figure 1 shows a graphical picture and a scanning electron microscope (SEM) image of the completed structure.

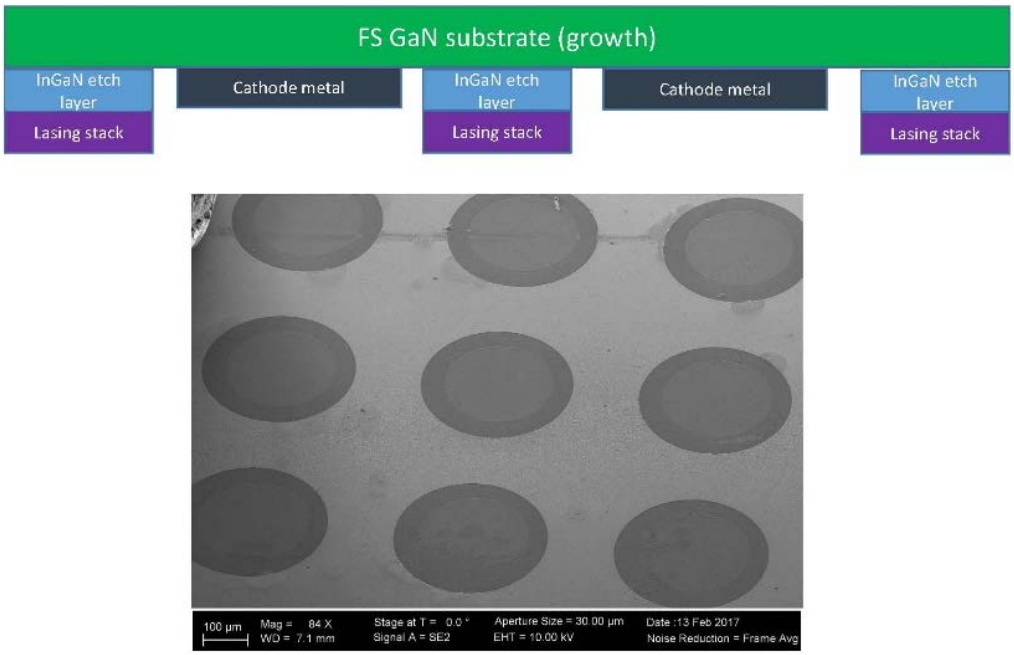

Fig. 1 Graphic (top) and SEM image (bottom) of the processed mesa array for GaN liftoff using an InGaN PEC etch layer

An advantage of this design, which contributes to the facile nature of the PEC process, is that the reaction is self-limited: there is no necessity to monitor the current or voltage or to run the process for a set amount of time. The process is finished and the reaction stops once the InGaN etch layer is completely consumed. There are 2 reasons for creating mesa structures for the PEC etch: 1) it allows for a region on which to apply the cathode metal and 2) it minimizes rate-limiting processes associated with undercutting a relatively large area.

The processed structure in Fig. 1 is adhered on a Teflon submount with Apiezon W (Black Wax) then placed an electrochemical cell filled with 0.1-M potassium hydroxide (KOH) electrolyte, with the processed mesas and cathode metal in contact with the solution. KOH is chosen as an electrolyte because it is relatively benign in the context of etching the cathode metal, and solvates III-nitrides more easily than acids.[9] The mesas are then illuminated by a 405-nm laser operating at 100 mW for the etching process. The reaction is left running for 8 h, occasionally refilling electrolyte that was lost to evaporation. A schematic of the process on the mount with a corresponding photograph is shown in Fig. 2. As the structure is illuminated in solution, the photogenerated holes in the PEC etch layer diffuse to the solution interface, where they drive an InGaN oxidation. The oxide is dissolved in solution. The corresponding photogenerated electrons diffuse to the cathode metal on which the hydrogen evolution is run.

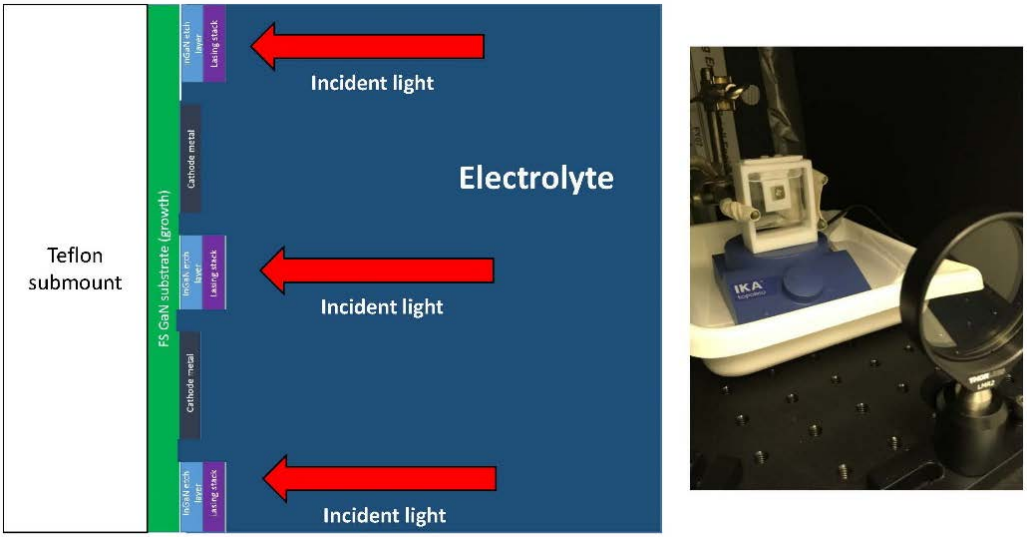

Fig. 2 Graphic (left) and photo (right) of the processed mesa array mounted on the electrochemical system to perform PEC etching liftoff

3 Results and Discussion

Figure 3 shows an SEM image of the mesa after the PEC etch process was run to completion. The interface between the substrate and the epitaxial GaN is clearly delineated as being etched, showing that this experiment successfully removed the InGaN PEC layer.

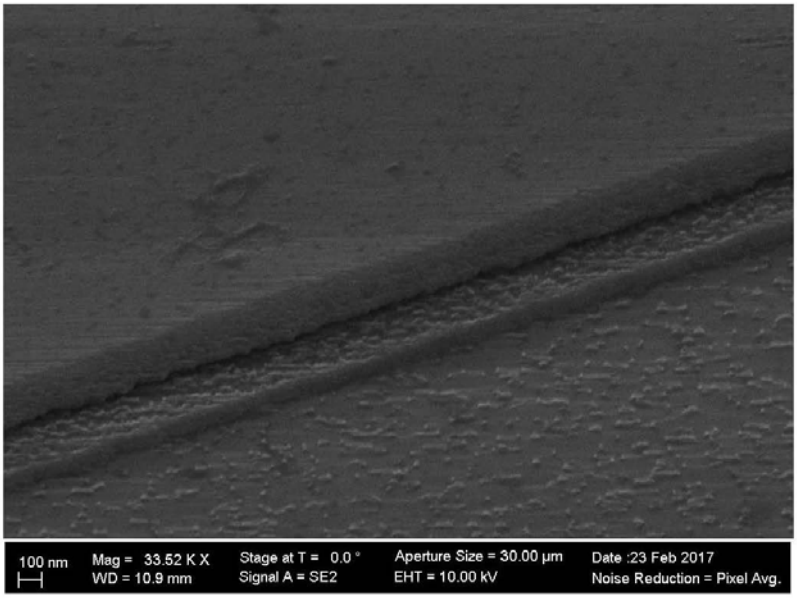

Fig. 3 SEM image of the mesa edge after the PEC etching process was run for 8 h

Two aspects of this experiment require further investigation. First, even though etching occurred across the PEC InGaN layer, the epitaxial GaN did not lift off. The initial thought was that 8 h was not enough time to fully undercut across the 200-µm-diameter mesa. The etch process was run for another 8 h, with the resulting SEM shown in Fig. 4, where the epitaxial layer remained. After the second etching process, the structures were subjected to sonication in acetone for 10 min. Partial liftoff of the epitaxial GaN on the mesa was achieved (Fig. 5), showing that the etch undercut was successful. However, much of the layer was not lifted off.

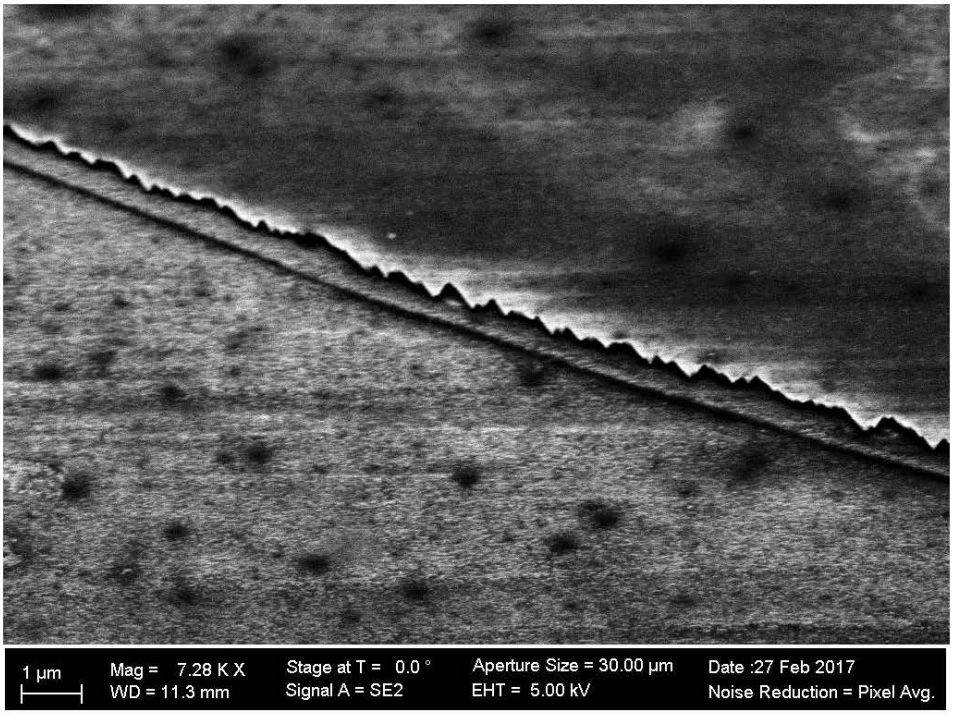

Fig. 4 SEM image of the mesa edge after the PEC etching process was run for 16 h

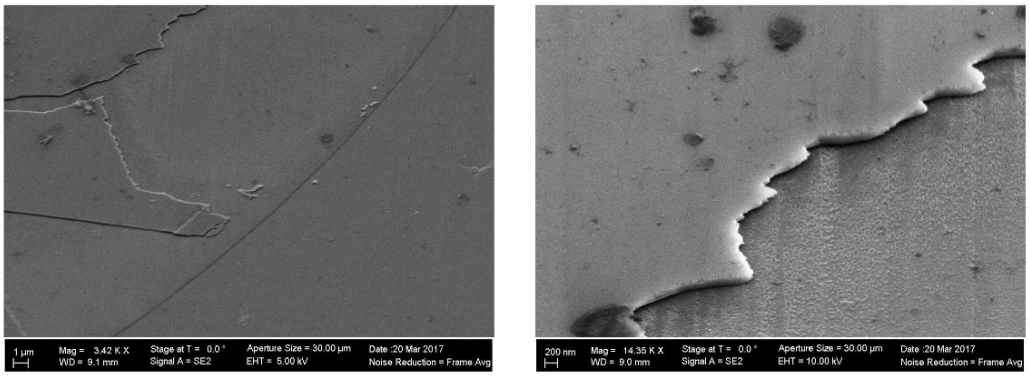

Fig. 5 SEM images of the mesa after sonication, showing partial liftoff near the edge as viewed zoomed out (left) and zoomed in (right)

This brings up the question as to whether the etch completely ran under the time of the experiment (16 h total). This is not likely the case, as the empty space within the etched layer is still viewable. The likely scenario is that mechanical forces or adhesion are preventing much of the liftoff process.

This problem can be addressed by prebonding the substrate onto which the material is to be transferred, as shown in Fig. 6. The bonded "sandwich" can then be mounted on the Teflon submount in the electrochemical cell, and as the etch proceeds, the mechanical forces from the bonding substrate can assist to pull off the epitaxial GaN from the PEC etch interface. This work is already in progress for using AlN for bonding between GaN and diamond.

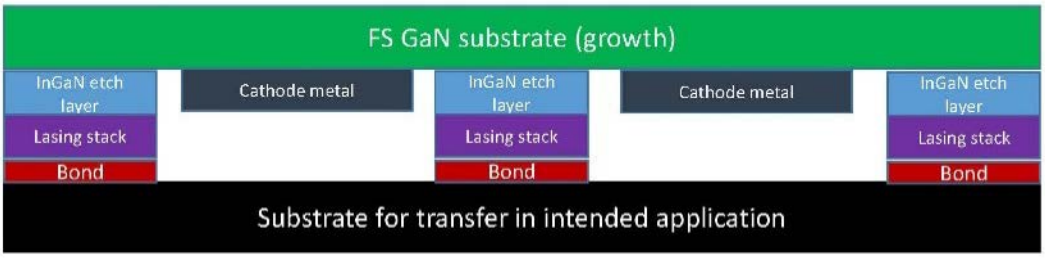

Fig. 6 Schematic of the prebonding of both substrates across the mesa array with PEC etch layer

The second aspect is that from the SEM images, the etching interface between the lifted-off GaN and the substrate is rough and serrated, which is not ideal for using epitaxial GaN for a lasing or electrical application, and is also not ideal in terms of reusing a substrate for future growth experiments. This interface is due to GaN being susceptible to a small amount of etching in an aqueous base solution, which has also been previously observed in PEC etching experiments.[4] This issue can be resolved by incorporating aluminum gallium nitride (AlGaN) as barrier regions around the InGaN PEC etch layer. Even a dilute amount of Al alloying improves AlGaN etch resistance. Therefore; the PEC etch process will produce clean interfaces that preserve the material quality of both the initial growth substrate and the transferred epitaxial film.

A final consideration is if the PEC etch layer requires optimization to effectively lift off the film above it in a reasonable time frame as well as achieving a clean break and a pristine surface in both the lifted-off film and the substrate. Bandgap engineering[7] has been shown to provide an improved method for etching near the materials interfaces, and using quantum wells[6] provides an alternative way to have a light absorber that etches in an electrochemical environment.

4. Summary and Conclusion

We have demonstrated a PEC etch process for epitaxial III-nitride materials by using InGaN as a sacrificial etch release layer that allows for the transfer of epitaxial GaN films from a growth substrate to a more appropriate substrate for the desired application. The scope of this project is to enable the use of a semipolar (20-21) GaN-based laser to be pumped with an electron beam for optical emission, but this process is versatile enough to enable III-nitride substrate transfer for a variety of electrical and optical applications. The range of materials is extended to most semiconductors provided the following criteria are met: 1) a lower bandgap alloy can be epitaxially integrated in the growth stack as an etch release layer and 2) a high-power optical source whose wavelength is such that the lifted-off stack is transparent, but the lower bandgap etch release layer is not.

This capability serves as a valuable processing step within the US Army Research Laboratory for a variety of research projects in which a substrate transfer of epitaxially grown materials is required. For each project, the specifics of etch chemistry, bonding, and other materials processing vary, but the setup created for this project can be applied to others as well.

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List of Symbols, Abbreviations, and Acronyms

Al_2O_3	aluminum oxide (sapphire)
AlN	aluminum nitride
AlGaN	aluminum gallium nitride
Au	gold
BCl_3	boron trichloride (gas)
Black Wax	Apiezon W
Cl_2	chlorine (gas)
GaN	gallium nitride
InGaN	indium gallium nitride
InN	indium nitride
KOH	potassium hydroxide
MBE	molecular beam epitaxy
MOCVD	metalorganic chemical vapor deposition
PEC	photoelectrochemical
SEM	scanning electron microscopy
Ti	titanium
UV	ultraviolet

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