Aluminium gallium nitride enables deep ultraviolet laser diodes

Mike Cooke reports on recent achievements of electrically- and optically-pumped devices, along with some developments in material processing.

Aluminium gallium nitride (AlGaN) is the key semiconductor alloy material in the present development of deep ultraviolet (UV) laser diodes (LDs) in the sub-300nm wavelength range. The first reports of working devices opens the way to new applications.

AlGaN alloys are wide-bandgap materials with potential for deep-UV light emission and for electronics that can sustain high electric fields and voltages before breakdown. The bandgap ranges from ~3.4eV (GaN) up to around ~6.2eV (AlN). These energy gaps correspond to photons with wavelengths from 365nm to 200nm, respectively.

The very short 100–280nm wavelengths of deep ultraviolet UV-C are able to disrupt biochemicals such as DNA, with the potential for disinfection, sterilization and water purification of bacterial and viral pathogens. UV-C emitting devices could also have a wide range of other, sometimes overlapping, applications: biochemical sensing/detection, small-particle detection, communications, optical storage, spectral analysis, medical treatment, and surface monitoring.

Here we look at the reports of UV-C laser diodes and optically pumped systems, along with some developments in AlGaN processing that could enable further UV-C laser diode progress.

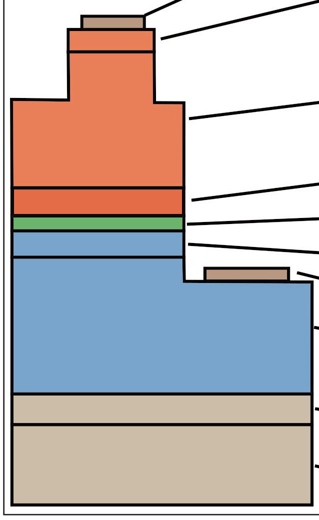

Figure 1. Schematic of fabricated UV-C laser diode structure.

Deep-UV laser diode

Researchers from Japan and the USA claim the shortest wavelength so far reported for current-injection laser diodes [Ziyi Zhang et al, Appl. Phys. Express, vol12, p124003, 2019]. The emission wavelength of 271.8nm places it in the UV-C range. Previous UV laser diode reports have been restricted to the 315–400nm UV-A field.

Asahi Kasei Corp and Nagoya University in Japan and Crystal IS in the USA collaborated on the device, which used low-dislocation-density AlN substrates to grow layers of AlGaN. Most reported short-wavelength laser diodes use silicon carbide, sapphire or free-standing gallium nitride.

The team used an unintentionally doped distributed polarization-induced doping cladding layer on the p-side, aiming for low internal loss, high hole conductivity and high hole injection. The usual magnesium doping of AlGaN has very poor performance in terms of generating mobile holes. Further, the use of ionized impurities creates scattering centers for light and charged carriers, which adversely impact performance.

The researchers grew the laser diode structure (Figure 1) on 2inch-diameter (0001) AlN substrates using metal-organic chemical vapor deposition (MOCVD). The dislocation density in the single-crystal substrate from Crystal IS was in the range 10^3–10^4/cm^2. The 9nm light-emitting single quantum well (QW) was designed to emit 270nm-wavelength UV-C light.

The 0.32µm distributed polarization doped (DPD) p-side cladding consisted of $Al_xGa_{1-x}N$ graded from 100% to 70% Al content. The grading effects a charge polarization gradient that generates and conducts mobile holes. The p-contact region consisted of magnesium-doped AlGaN further graded down to pure GaN. The n-side of the device was doped with silicon using an impurity concentration of more than $1x10^{19}/cm^3$ in both contact and cladding layers. The epitaxial layers were strained pseudomorphically with the underlying AlN substrate.

Laser diode devices were fabricated with 4μm-wide ridge waveguides. The ridge etch exposed the n-contact layer on which vanadium-based metal was deposited. Silicon dioxide passivation was applied before the n-contact metal. The p-contact and other wiring and probe pads consisted of nickel/gold metal.

The fabricated laser diodes were cleaved along the <$11\bar{2}0$> direction into 400μm-long cavities. The resulting ($1\bar{1}00$)-plane facets were coated with five dielectric layer pairs consisting of hafnium dioxide and silicon dioxide. The reflectivity of the coatings were more than 90%, according to the researchers. The high reflectivity was a key factor in reducing threshold current.

The laser diodes were tested under pulsed operation with 50ns width and 0.01% duty cycle. The light output power increased non-linearly at around 0.4A injection, $25kA/cm^2$ density relative to the p-electrode area. Above this threshold a sharp spectral peak emerged around 271.8nm wavelength. The threshold occurred with a forward voltage of 13.8V.

The optical polarization of the emission was transverse electric (TE): while the transverse magnetic (TM) component had a constant 11nm full-width at half maximum (FWHM) between 0.2A and 0.5A, the TE values were 6.6nm and 0.41nm, respectively (Figure 2).

The researchers attributed the 'remarkably low' threshold voltage of 13.8V to the DPD structure giving a flat valence-band profile on the p-side, allowing injection of the holes without a barrier. They also speculate that the high-Al-content material on the p-side of the waveguide layer created an electron-blocking barrier in the conduction band.

The team comments: "The pseudomorphic growth of the whole structure, including the DPD on the single-crystal AlN substrate, maximized the polarization-induced charge to achieve high hole conductivity, considering that relaxation of the graded structure can also hinder polarization doping."

One problem was found in the MOCVD growth process: convex, hexagonal pyramid-shaped hillocks on the surface with a density of $6x10^3/cm^2$. The hillocks seemed to contribute an additional emission peak around 278nm wavelength. In devices that included one of these hillocks, lasing was not achieved.

Based on transmission electron microscope analysis, the researchers believe that the hillocks originate from pre-existing threading dislocations in the AlN substrate. Threading dislocations offer non-radiative routes to carrier recombination and can adversely affect current flow patterns.

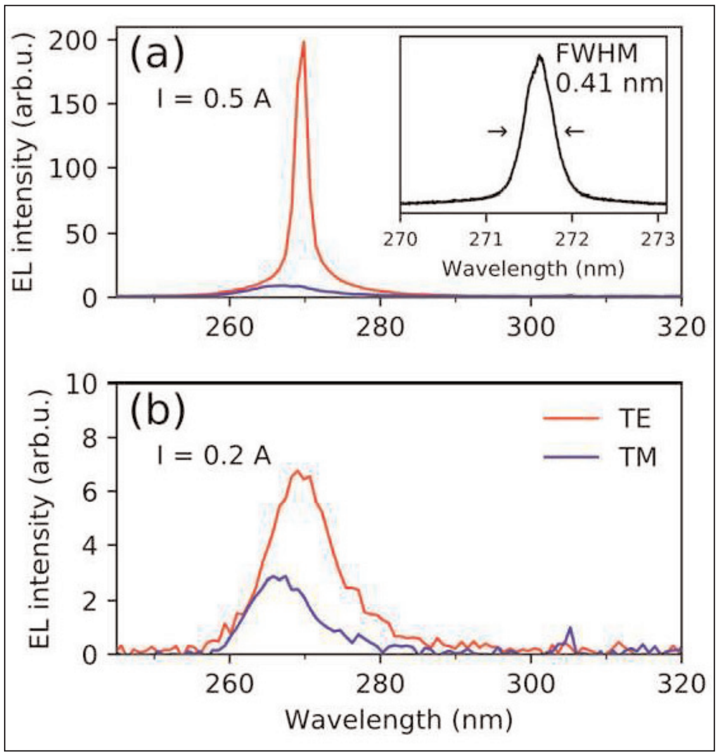

Figure 2. Edge-emission spectra with TE and TM polarization at (a) 0.5A and (b) 0.2A forward current. Inset in (a) shows spectrum of TE mode at 0.5A with highest wavelength resolution.

For lasing, the hillocks also affect the optical structure, scattering light out of the waveguide mode. "A high-quality AlN substrate with low dislocation density appears to be fundamental to the development of a UV-C LD," the team concludes.

Optically pumped lasing

Researchers in China shortly before presented a deep-UV (DUV) 249nm optically pumped III–nitride laser structure based on gallium nitride rather than the more usual wider-bandgap AlGaN QWs [Maocheng Shan et al, ACS Photonics, vol6, p2387, 2019]. The very short wavelength of 249nm was enabled by the extreme confinement of very thin GaN wells in thin AlN barriers. The corresponding photon energy was 5.0eV, a couple of eV higher than the ~3.4eV bandgap of bulk GaN.

The team from Huazhong University of Science and Technology in China, Saudi Arabia's King Abdullah University of Science and Technology (KAUST) and Ningbo Institute of Materials Technology and Engineering in China reports that previously only spontaneous emission has been achieved in GaN/AlN multiple quantum well (MQW) systems.

Among the problems for AlGaN DUV lasers are strong quantum-confined Stark effects (QCSEs) arising from electric fields, based in ionic charge polarization, that pull electrons away from holes, inhibiting recombination into photons. Also, high-Al-content AlGaN tends to emit radiation optically polarized in a TM mode, which

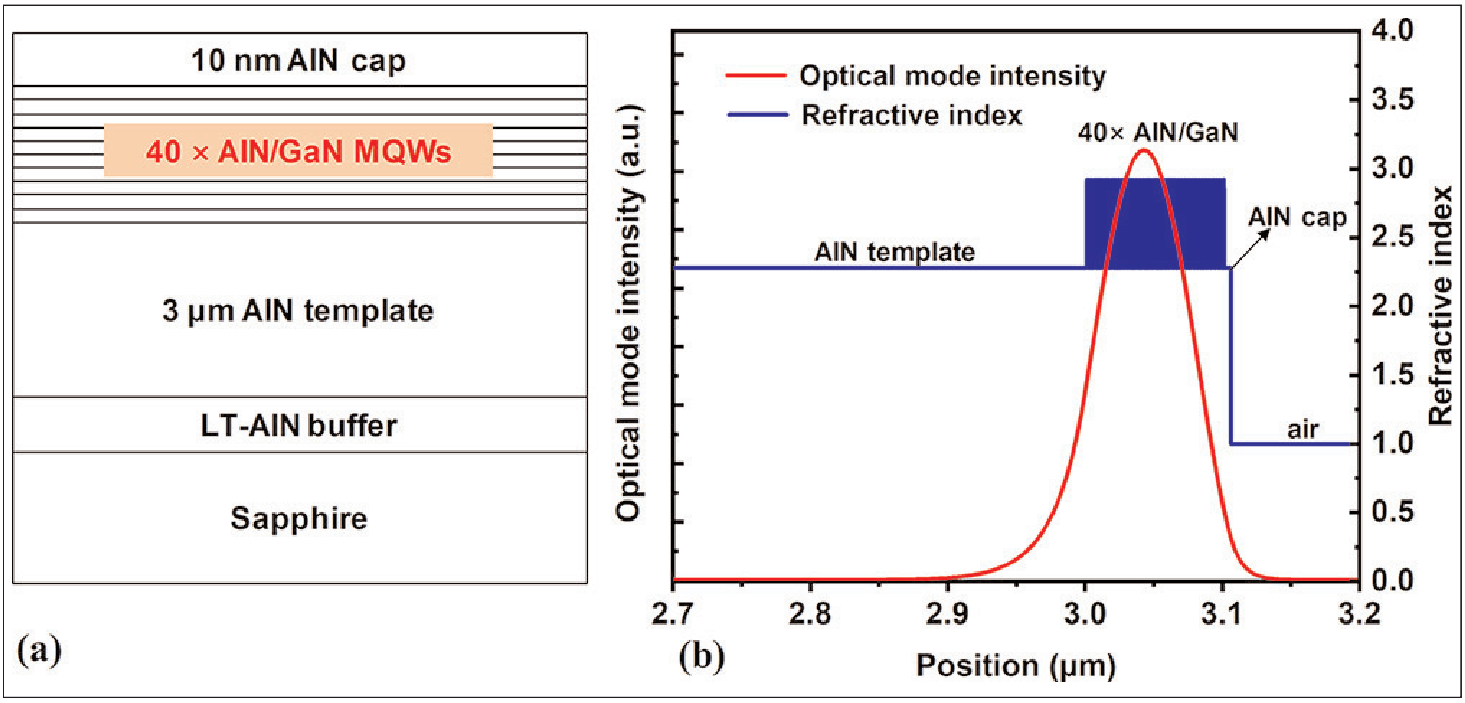

Figure 3. (a) Schematic diagram of AlN/GaN MQW DUV laser grown on sapphire substrate; (b) simulated optical mode profile and refractive index distribution.

is more difficult to use efficiently in light-emitting diode and edge-emitting laser structures.

MOCVD on two-inch c-plane sapphire resulted in an AlN/GaN MQW laser structure (Figure 3). The 750ºC low-temperature (LT) AlN buffer was 15nm thick. The 3μm AlN template layer was grown at 1230ºC. X-ray rocking curve analysis suggested that the AlN template was of higher crystalline quality than previously used for AlGaN DUV laser structures.

A somewhat lower growth temperature of 1040ºC was chosen for the MQW to ensure high-quality wells, avoiding evaporation of the more volatile GaN material. The GaN wells were designed to be 4 monolayers (MLs) thick, while the AlN barriers were 6MLs. In metric measurements, according to x-ray analysis, the wells and barriers were 1.0nm and 1.5nm thick, respectively.

The similarity of the QW and barrier (QB) thicknesses was expected to lead to a higher refractive index, compared with the usual situation with significantly thicker barriers. The researchers explain the use of 40 wells as being "due to comprehensive considerations of the lateral optical confinement, penetration depth of the excitation laser beam, gain medium volume, strain relaxation, and material and interface quality."

The final 10nm AlN cap was to provide surface passivation. The team says that ideally the top AlN layer would be thicker to provide a more symmetric waveguide effect coupled with the underlying AlN template. The reason for the thinness was to enable pumping from a 193nm argon fluoride (ArF) excimer laser with minimal absorption losses.

Optical simulations of the structure suggested a 35.4% confinement factor. The researchers explain: "The large factor was partially attributed to the use of high-index GaN QWs and large MQW pair number of 40. Also, it is partially caused by the comparable thicknesses between the GaN QWs and the AlN QBs, resulting in a larger average index."

The material was prepared into 1mm-long cavity laser bars by thinning the sapphire substrate, and laser scribing and cleaving. No optical coating was applied to the facet.

The laser pump was pulsed at 50Hz with 5ns duration. The emission peak was at 249nm with little shift between spontaneous and lasing operation (Figure 4). The researchers attribute this to a minimal QCSE, resulting from the thinness of the GaN QWs.

The team puts the lasing threshold at 190kW/cm^2 pumping power density. The researchers report that this is comparable to AlGaN-based DUV laser structures on sapphire or AlN substrates. "Such a threshold can be mostly attributed to the high material and interface quality, large quantum and optical confinement, and smooth cleaved facet," they write.

As the system passed through the laser threshold, the linewidth reduced from 8nm to 0.2nm FWHM. Above and below threshold the degree of optical polarization was 0.92 and 0.48, respectively. The polarization here was the ratio of the TE intensity excess over the TM to the total intensity (that is, $(I_{TE}-I_{TM})/(I_{TE}+I_{TM})$).

The researchers explain the favoring of TE polarization: "The TE dominance is caused by the topmost position of the heavy hole (HH) band of GaN and thereby the optical transition between the conduction band and the HH band."

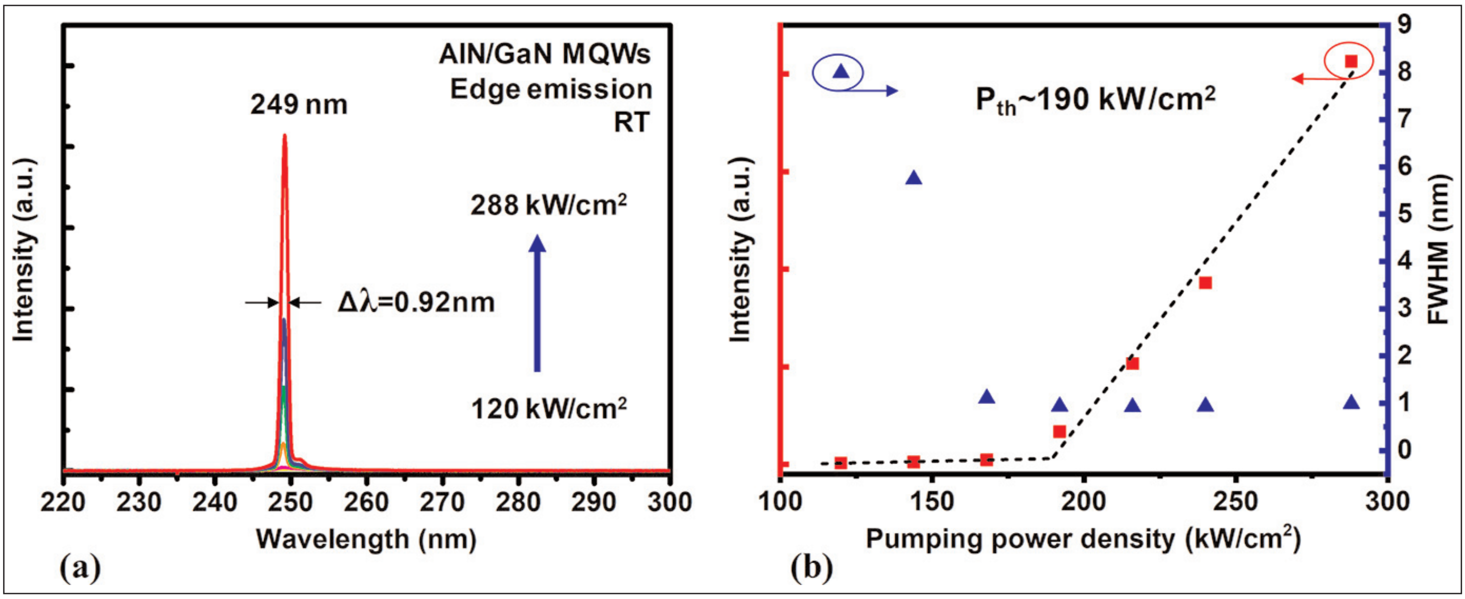

Figure 4. (a) Laser emission spectra and (b) peak intensity and line width of spectra as function of pumping power density.

The even greater favoring of TE emission above laser threshold is attributed to a large TE-to-TM gain ratio in stimulated operation.

Electrochemical membrane release

Moving on to AlGaN processing technology advances, researchers from Sweden and Germany have been developing electrochemical etching as a means to create thin-film AlGaN optoelectronic and power-electronic devices [Michael A. Bergmann et al, Appl. Phys. Lett., vol115, p182103, 2019].

The researchers from Chalmers University of Technology in Sweden, Technische Universität Berlin in Germany and KTH Royal Institute of Technology in Sweden comment: "Heterogeneously integrated AlGaN epitaxial layers will be essential for future optical and electrical devices like thin-film flip-chip UV light-emitting diodes, UV vertical-cavity surface-emitting lasers, and high-electron-mobility transistors on efficient heat sinks."

Releasing the AlGaN layers from the epitaxial growth substrate would enable vertical cavities with dielectric applied to both sides of a membrane. However, present methods for releasing AlGaN such as laser lift-off tend to damage the material, reducing performance in the final device.

The researchers first grew a $2x10^{18}/cm^3$ silicon-doped $Al_{0.5}Ga_{0.5}N$ layer on c-plane sapphire with an AlN template layer using a close-coupled showerhead MOCVD reactor (Figure 5). The n-type conductivity from the silicon doping ensured current spreading for uniform electrochemical etching.

The current-spreading layer was followed by a 225nm $0.5x10^{18}/cm^3$ lightly silicon-doped $Al_{0.5}Ga_{0.5}N$ etch-stop layer. The sacrificial layer for membrane release was 130nm $2x10^{19}/cm^3$ heavily Si-doped $Al_xGa_{1-x}N$. The membrane layer was 580nm (1900nm for $Al_{0.11}Ga_{0.89}N$ sacrificial layer sample) unintentionally doped $Al_{0.5}Ga_{0.5}N$.

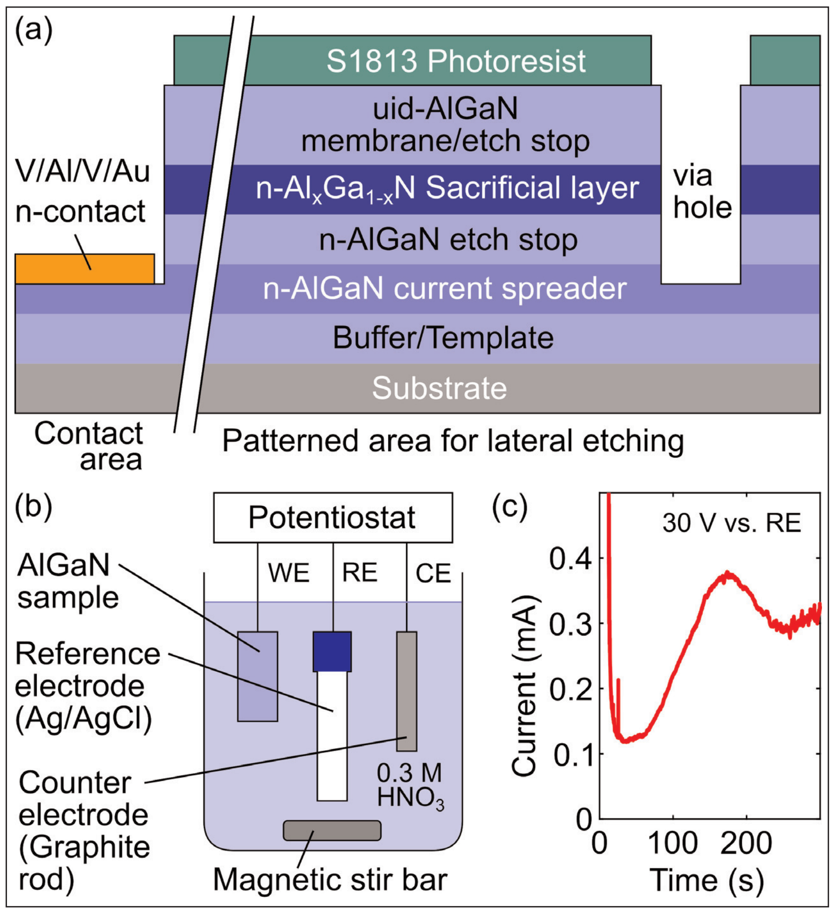

Figure 5. (a) AlGaN sample structure, (b) three-electrode setup for electrochemical etching, and (c) etching current versus time for etching $Al_{0.11}Ga_{0.89}N$ sacrificial layer at 30V.

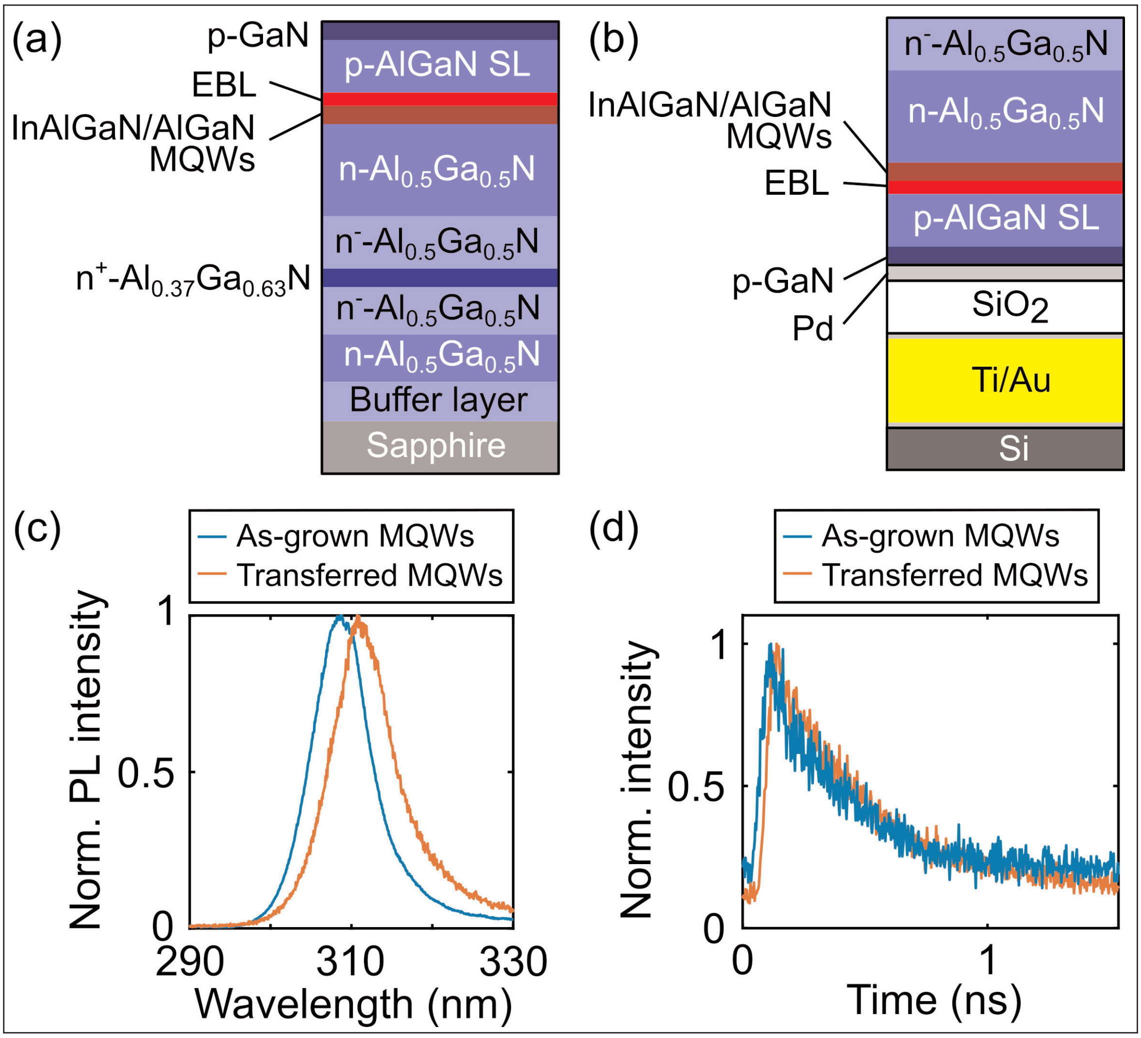

Figure 6. (a) As-grown MQW sample structure, (b) transferred structure, (c) PL spectrum of as-grown MQW probed from Ga-polar side and transferred structure probed from etched N-polar side, and (d) time-resolved PL of structures.

The electrochemical etch was found to proceed isotropically around the etch holes, creating an air gap between the substrate and membrane. Eventually the etch fronts merged. With an $Al_{0.5}Ga_{0.5}N$ sacrificial layer, an etch potential of 30V resulted in smooth surfaces on the upper and lower etch-stop layers. At the lower potential of 25V some residues were left on the etch-stop layers. Even lower potentials of 20V and 15V resulted in increasingly porous sacrificial layers.

The researchers attribute the etching to the generation of holes at the AlGaN/electrolyte interface from Zener tunneling or avalanche breakdown in a depletion region. "These holes oxidize AlGaN at the interface, and the oxidized material can be dissolved by the electrolyte," the team explains. The researchers propose a chemical reaction equation:

$$2Al_xGa_{1-x}N + 6h^+ \longrightarrow 2xAl^{3+} + 2(1-x)Ga^{3+} + N_2.$$

Atomic force microscopy on the etched surface of a membrane transferred to a silicon carrier had 3.5nm root-mean-square (RMS) roughness on a 1µm x 1µm area. The sacrificial layer used for the electrochemical etch was $Al_{0.27}Ga_{0.73}N$.

A MQW structure was grown on a 130nm $Al_{0.37}Ga_{0.63}N$ sacrificial layer to show that the electrochemical etch could be used without affecting device performance (Figure 6). The $2x10^{18}/cm^3$ silicon-doped $Al_{0.5}Ga_{0.5}N$ 4mm-thick underlayer was relaxed. The sacrificial layer aluminium content was chosen to be transparent for photoluminescence (PL) analysis but low enough to contrast with surrounding layers.

The MQWs were indium aluminium gallium nitride with 21% Al content. The three wells were 2nm thick, separated by 5nm $Al_{0.3}Ga_{0.7}N$ barriers. The magnesium-doped p-type layers were an $Al_{0.75}Ga_{0.25}N$ electron-blocking layer, an AlGaN superlattice (SL), and a 20nm p-GaN cap layer.

X-ray analysis showed that the $Al_{0.5}Ga_{0.5}$:Si was 'pseudomorphic' — i.e. strained — on all sacrificial layer compositions.

The electrochemical etching was enabled by dry reactive-ion etching 10µm-diameter via holes in a 7x9 400µm-pitch array to expose the sacrificial layer. The etched holes reached down to the current-spreading layer. The electrochemical contact with the current-spreading layer was made through an electron-beam-evaporated and annealed vanadium/aluminium/vanadium/gold metal stack. The top-side of the membrane was protected from etching damage with a 1.3µm photoresist layer.

The electrochemical etch used three electrodes in 0.3M nitric acid electrolyte, which was constantly stirred with a magnetic bar. The AlGaN 'working electrode' was kept at a constant positive potential relative to the silver/silver chloride (Ag/AgCl) 'reference electrode'. Control of the process was through a graphite rod 'counter electrode', which allowed the current flow to vary in the low-milliamp range. The samples were 5mmx10mm.

The material was prepared for electrochemical etching by dry reactive-ion etching circular mesas. Palladium was deposited on the p-GaN cap. The mesas were partially covered with 1µm sputtered silicon dioxide (SiO_2) to prevent parasitic etching during the electrochemical process. Finally, a titanium/gold bond pad was deposited on the palladium.

The electrochemical etch potential was 25V. The released structures were transferred to silicon carriers with titanium/gold bonding layer using a 300ºC thermos-compression process.

The PL analysis showed a small red-shift after transfer. The researchers report "This shift of 2nm could be caused by small local variations in the Al composition and thickness over the sample, residual strain in the epitaxy, and process induced strain."

Time-resolved measurements before and after transfer showed the same PL decay rate of 340ps. The team concludes: "This confirms that the electrochemical etching and transfer process do not influence the quality of the QWs and, hence, are an appropriate process for fabrication of devices based on free-standing membranes."

Metal-organic growth on silicon carbide

University of California Santa Barbara (UCSB) in the USA has improved MOCVD AlN growth on silicon carbide (SiC) with a view to AlGaN DUV light-emitting diode and optoelectronics fabrication [Christian J. Zollner et al, Appl. Phys. Lett., vol115, p161101, 2019].

The work was aimed at providing crack-free AlN templates for AlGaN growth with low threading dislocation density without using costly and time-consuming approaches such as pulsed lateral overgrowth or growing very thick (>10µm) buffer layers.

The researchers comment: "Combining overall improvements in AlN MOCVD techniques, improved SiC wafer quality, and growth-mode control concepts demonstrated in MBE, we find that MOCVD growth of AlN/SiC is a viable route to high-quality UV-LED template layers."

The team also points out that there are highly selective dry etch techniques for efficient SiC substrate removal, raising the prospect of high-efficiency DUV-LED fabrication. Such removal would be necessary since SiC is highly absorbing of these high-energy DUV photons. In fact, SiC becomes absorbing around 380nm.

Although AlN can be grown on much lower-cost sapphire, which is transparent to DUV, the advantage of SiC is that it is a much better match in terms of crystal structure. The researchers also point out that "there is no risk of inadvertent nitrogen-polar growth on the substrate's Si-face." At present, deep-UV LEDs exhibit low wall-plug efficiency due to a number of factors, one of which is the presence of threading dislocations.

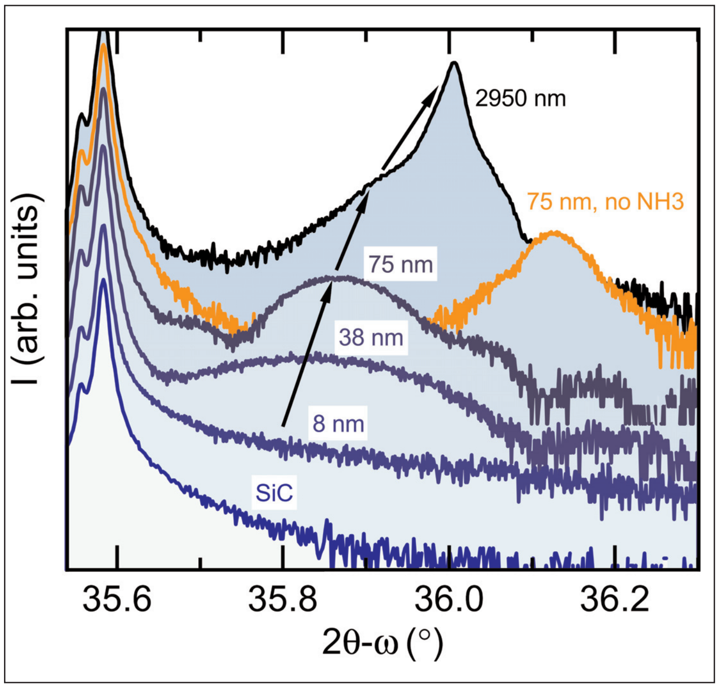

Figure 7. Symmetric triple-axis 2ω–θ x-ray diffraction scans of AlN/SiC films, with SiC double-peak (blue) for reference. Growth sequence with (black) and without (orange) ammonia pretreatment compared up to 75nm, along with full 2.95µm AlN thickness template (black). Logarithmic intensity scale.

A 250nm AlN initiation layer was grown at 1200ºC, followed by 2.7µm AlN at 1400ºC. The growth rates were 1.5Å/s and 6Å/s, respectively. The two-step process targeted reduced numbers of threading dislocations and a smoother surface.

The 4H SiC substrates came from two suppliers. The 'sample A' substrate was mechanically polished with polishing marks obscuring the atomic steps typically produced during the crystal growth process. In 'Sample B', which had a smoother surface from chemical-mechanical planarization (CMP), these steps were visible in terraced surface structures. Samples A and B were 250µm and 500µm thick, respectively.

AlN films grown on sample B were found to have reduced tensile stress and less cracking. "The marked reduction in tension when switching to smooth substrates suggests that small island size is a primary driver of stress generation on rough substrates," the team comments.

A 10 minute ammonia pretreatment of sample B at 1400ºC for 10 minutes changed the slight tensile stress to strong compression with a value of −1.1GPa. The surface was also crack-free up to a 5µm scale. X-ray rocking curves also showed reduced FWHM diffraction peaks, suggesting higher film quality (Figure 7).

One effect of the pre-treatment was to increase the spacing of the atomic steps from 165nm to 330nm.

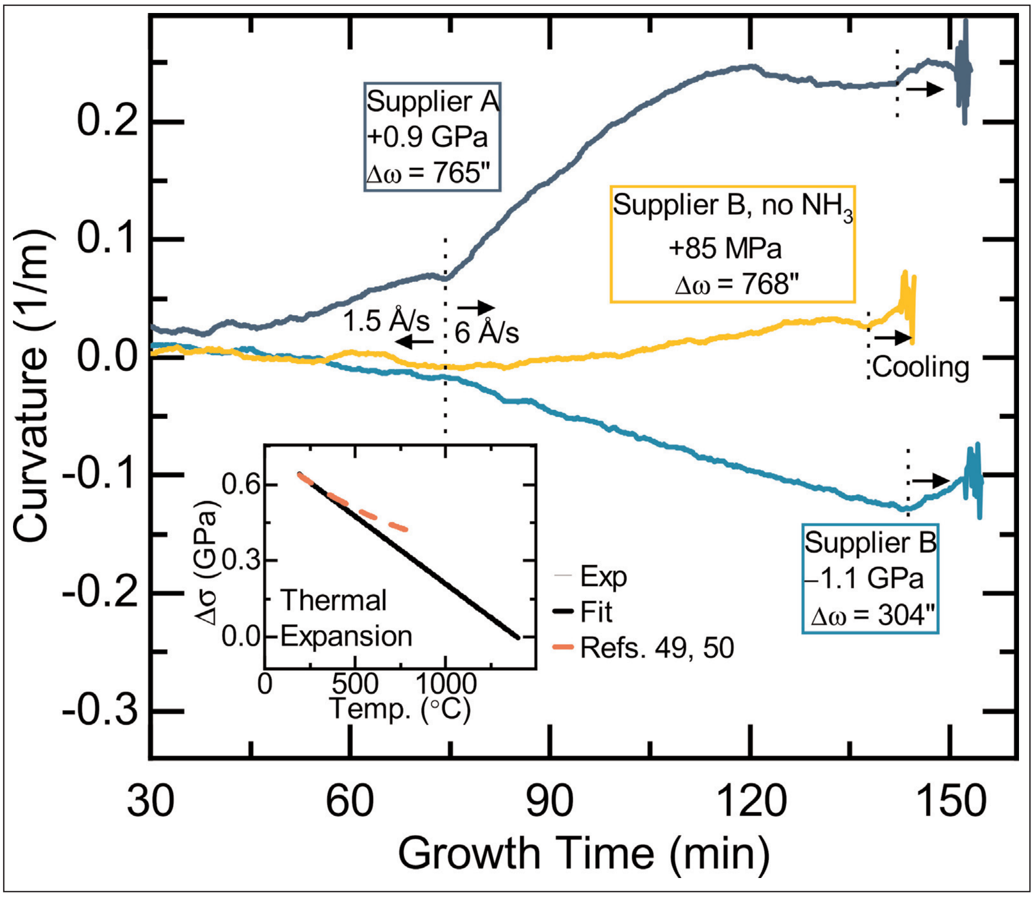

Figure 8. In situ curvature of AlN template on three substrate types: rough SiC with ammonia pre-treatment (top, tensile), smooth substrate (middle, weakly tensile), and smooth substrate with ammonia treatment (bottom, highly compressive). Growth stress and $20\bar{2}1$ FWHM, Δω, listed. Inset: thermal expansion mismatch stress: data (gray) compared with literature models (red, dashed) and linear least squares fit (black, solid).

The shorter step distance in the initial surface has been found to increase threading dislocation density and to create lattice stacking mismatch problems.

Laser monitoring of the substrate curvature during growth (Figure 8) suggested a thermal expansion coefficient mismatch in sample B of 1.13×10^{-6}/ºC, which resulted in a slight increase in lattice mismatch of 0.15% at 1375ºC. A thick AlN layer is fully relaxed at its growth temperature, but on cooling to room temperature develops tensile stress of ~700MPa that can lead to cracking.

Plan-view transmission electron microscopy gave a threading dislocation density value of $2.4\times10^{8}/cm^{2}$. ■

The author Mike Cooke has worked as a semiconductor and advanced technology journalist since 1997.