Patterned sapphire for nitride enhancements

In the past few years, patterned sapphire substrates have been used to improve performance of nitride semiconductor light-emitting devices. Mike Cooke reports on some recent developments.

Many researchers are seeking low-cost ways to enhance the performance of nitride semiconductor light-emitting diodes (LEDs) and other devices. One technique for this has been to pattern the sapphire substrate used before nitride growth. These nano-scale patterns can have a number of effects to improve the performance of the resulting LEDs, affecting the ability to create photons from electron–hole recombination and the ability of these photons to be extracted from the device.

For example, the nanopatterned surface can affect the nitride semiconductor growth process, reducing the number of dislocations in the nitride semiconductor crystal; such dislocations can degrade LED performance. Also, the growth process often creates air-voids at the interface between the sapphire and nitride semiconductor heterostructure; the voids can be used to alter the way the light generated by the LED action leaves the device.

Another device type for which these improvements have been used is photovoltaic power generation from reversing the diode action. In principle, nitride semiconductors could cover a wide range of the solar spectrum from the infrared (InN, bandgap 0.7eV ~1800nm) to ultraviolet (AlN, 6eV ~200nm) wavelengths. In practice, the nitride semiconductor PV devices produced so far have tended to have low conversion efficiency, being restricted in the main to the ultraviolet region (less than 400nm) where there are fewer solar photons.

The problems in moving to longer wavelengths are similar to those in green LEDs and laser diodes — relatively poor material quality due to composition fluctuations arising from the tendency of the indium component needed for longer wavelength response not mixing well with other nitrides; and complications due to polarization fields arising spontaneously and due to the large piezoelectric strain-dependent effects in nitrides.

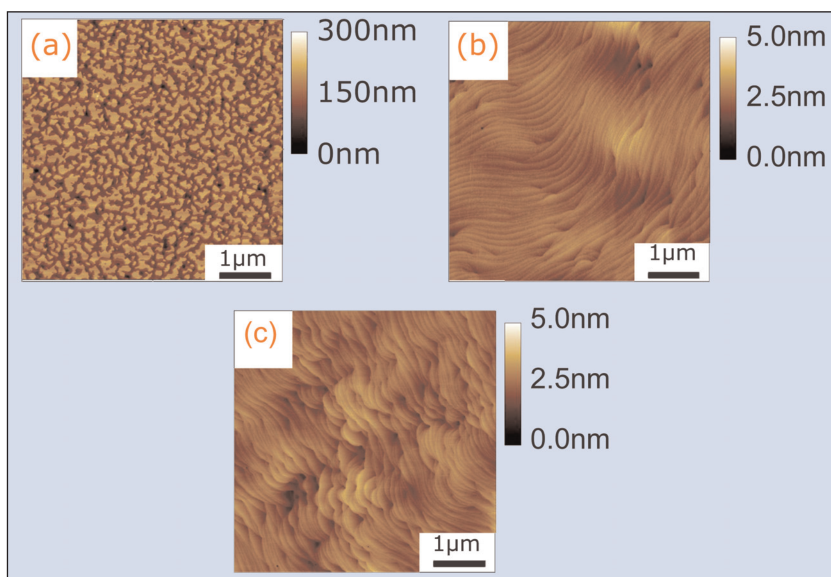

Figure 1. AFM images of surfaces of (a) sapphire with void-embedded cortex-like nanostructure (VECN), (b) undoped gallium nitride (u-GaN) on VECN sapphire, (c) u-GaN on conventional sapphire. Scan area is 5µm x 5µm.

Nanopatterning for light emission

Taiwan-based researchers have developed a sapphire nanopatterning technique that increases external quantum efficiencies (EQE) of nitride semiconductor LEDs 2.4x over devices grown on conventional sapphire at 20mA drive current [Yu-Sheng Lin and J. Andrew Yeh, Appl. Phys. Express, vol4, p092103, 2011].

The researchers at National Tsing Hua University and National Applied Research Laboratories comment that the EQE of 58.3% at 20mA is comparable with that of other reported devices on nanopatterned sapphire substrates with values in the range 40–50%. The conventional device had an EQE of 24.5%. The output power measured from the top side of the devices at 20mA was 33.1mW for the patterned device and 13.9mW for the conventional LED.

The Taiwan researchers used a random nanopattering they called 'void-embedded cortex-like nanostructures' (VECN). The team sees their method as being "a cost-effective solution" for producing wafer-level cortex-like

nanostructures on sapphire for high-efficiency LEDs without the need for an expensive semiconductor mask.

The nanopatterning of the sapphire wafer surface was achieved by creating a 2μm-thick hard mask of polysilicon and performing an inductively coupled plasma reactive-ion etch with a boron tetrachloride and chlorine mix. The deposition of the polysilicon was through 640ºC low-pressure chemical vapor deposition.

The patterning for the hard mask was created by dipping the polysilicon-covered wafer in diluted Wright-etch solution for 30 minutes. Wright-etch solution is an acid mix developed in the 1970s to reveal defects in silicon crystal structures. The hard mask was removed by potassium hydroxide solution at 80ºC. The resulting patterning of the sapphire wafer surface consisted of $10^{10}/cm^2$ 80–150nm deep structures spaced 50–150nm apart (Figure 1).

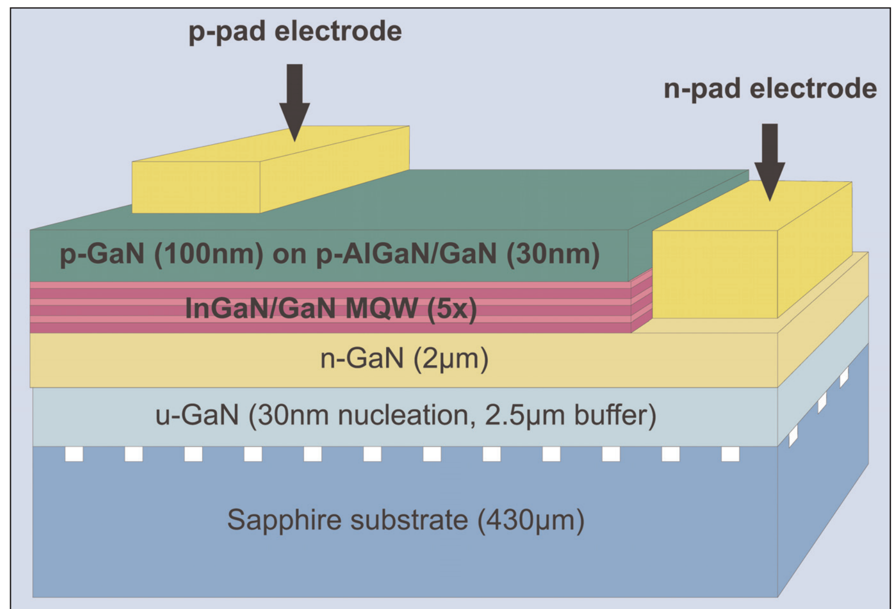

Figure 2. Schematic diagram of LED-VECN structure. The p-side layers consist of 30nm aluminum gallium nitride/gallium nitride (AlGaN/GaN) superlattice and 100nm p-GaN.

The LED structures were grown using low-pressure metal-organic chemical vapor deposition (Figure 2). Atomic force microscopy (AFM) of the buffer layer suggested a pit density of 10^7–$10^8/cm^2$. This is two orders of magnitude lower than pit density values for gallium nitride (GaN) grown on conventional sapphire substrates (CSS). Such pits are attributed to threading dislocations that propagate from the sapphire to the top of the GaN surface.

X-ray diffraction (0002) rocking curve full-width at half maximum (FWHM) values of 211 arcsec for the nanopatterened GaN/sapphire, compared with 294arcsec for GaN on conventional sapphire substrates (GaN/CSS) also suggest improved crystal quality. The further LED layers slightly increased the FWHM for the nanopatterned device structure to 216arcsec, while the CSS device structure FWHM decreased to 256arcsec. Satellite peaks up to fifth order were detected, suggesting good layer periodicity for the indium gallium nitride/gallium nitride (InGaN/GaN) multi-quantum wells (MQW), which made up the active light-emitting region of the device.

The electroluminescent peak occurred at 438nm (violet) at 20mA drive current (Figure 3). At 20mA, the patterned LED had a lower forward voltage of 3.6V, compared with the conventional device's 3.8V. The reflection from the GaN/sapphire interface was 32.8% higher in the patterned device compared with that on conventional sapphire. The reflection is thought

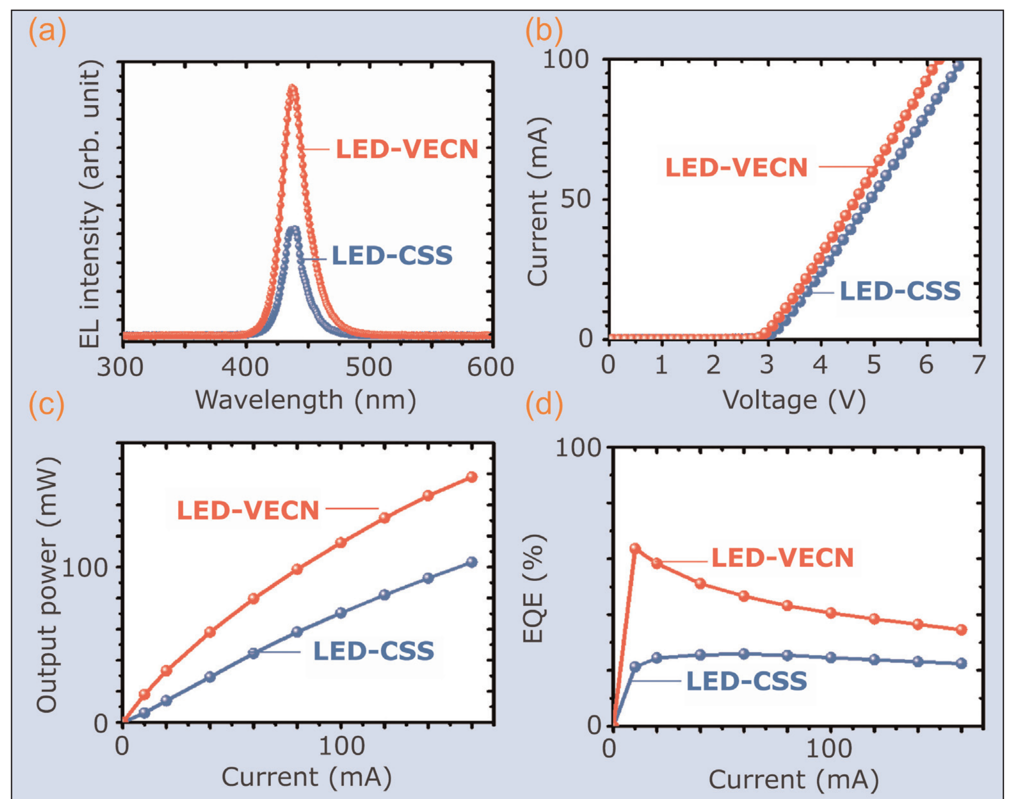

Figure 3. (a) Electroluminescence spectra for LED on VECN and conventional (CSS) substrate located at 438nm under an injection current of 20mA. (b) Current–voltage (I–V) curves of the LED-VECN and the LED-CSS, (c) light output power, and (d) EQE in relation to current characteristics of LED-VECN and LED-CSS, respectively.

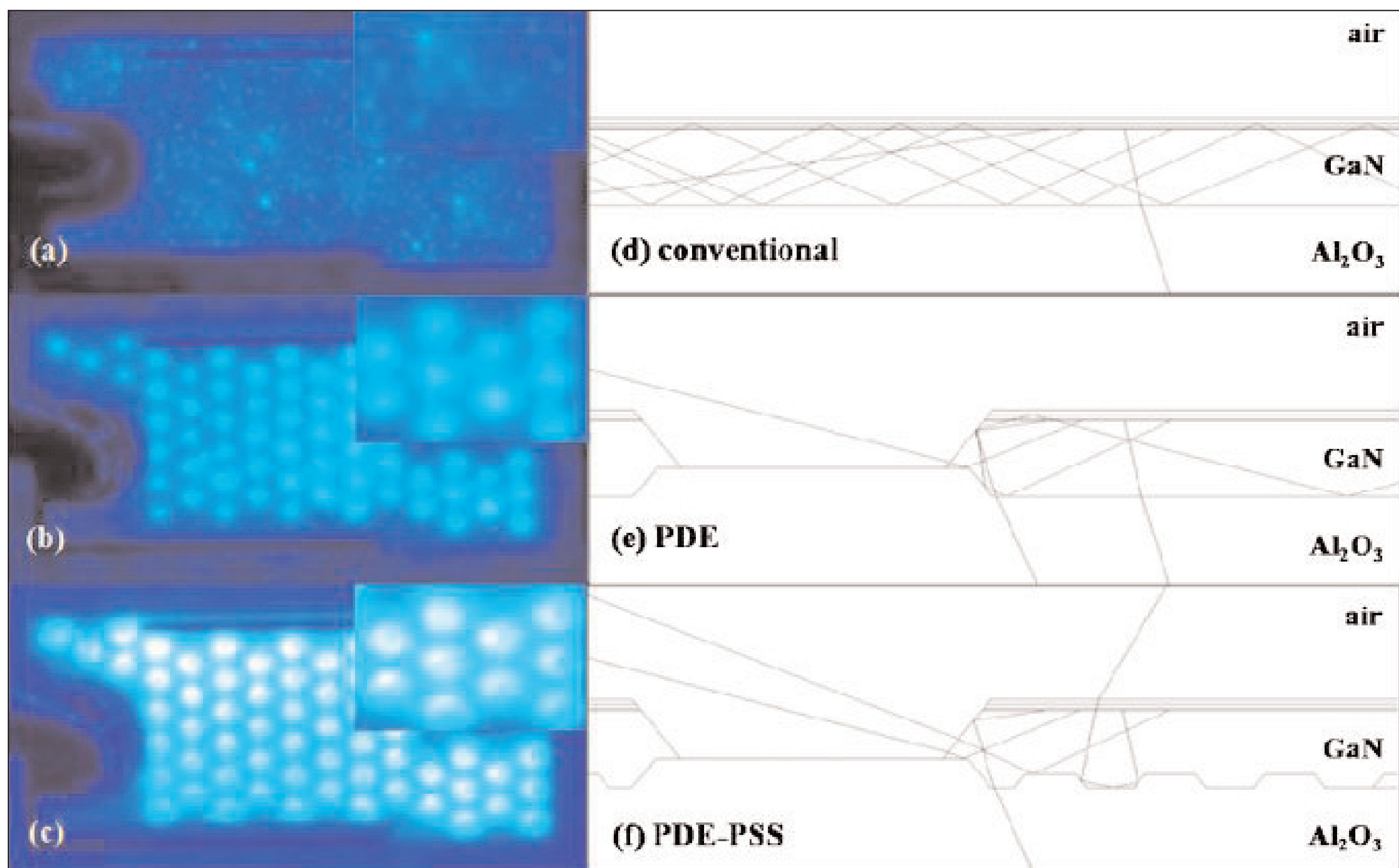

Figure 4. Electroluminescence images of (a) conventional, (b) PDE-only, and (c) PDE-PSS LEDs at low current. Figures (d)–(f): ray-tracing diagrams of the respective LEDs.

to occur at air voids formed during the GaN growth. Such reflection occurs due to the large difference in refractive index between GaN (2.45) and air (~1).

The characterizations of the crystal structure and light reflection suggest that the improvement results from both reduction in dislocation density, and improved light extraction through reflection.

In Korea, Chonbuk National University and LG Display [Hyun Kyu Kim et al, Jpn. J. Appl. Phys., vol50, p042102, 2011] have combined a periodic deflector embedded on patterned sapphire substrates (PDE-PSS) to enhance light output. A 100nm-thick silicon dioxide mask was patterned and wet etched using photolithography and buffered sulfuric/phosphoric acid solution. The pattern consisted of hexagons that were either 15μm diameter with 25μm periodicity or 3μm diameter with 15μm periodicity. The advantage of a wet process is avoidance of damage that arises from plasma etches.

LED structures were produced that consist of 315μm x 315μm mesas with a nickel-gold transparent conductive layer, and chromium-gold n-type and nickel-gold p-type contacts.

The researchers attribute a lower forward voltage of 3.45V at 20mA in their LEDs grown on PDE-PSS substrates to the avoidance of plasma damage. LEDs grown on non-patterned sapphire — both conventional planar sapphire, and with PDE structures, but without PSS — exhibited forward voltages of 3.6V at 20mA. Patterning also tightened the peaks of x-ray diffraction rocking curves from 368 arcsec (planar) and 300 arcsec (PDE-only) to 270 arcsec (PDE-PSS). For the final pay-off in terms of light output power at 20mA, the PDE-only device emitted 40% more than a conventional planar device, while the PDE-PSS LED produced 60% more light.

The researchers comment on the light extraction: "This result implies that the polygonal holes play a role as guided light deflectors, which facilitates the multiple chances for photons to escape from the LEDs. In addition, [Figure 4] shows that the light intensity around the polygonal holes of the PDE-PSS LEDs is brighter compared to the intensity around the polygonal holes in the PDE LED. We also observe a strong luminescence emanating in the perimeter of polygonal hole and in the polygonal hole inside as well."

Earlier this year, researchers from Rensselaer Polytechnic Institute (RPI) in the USA and SCIVAX Corp of Japan used patterned sapphire substrates to improve the efficiency of green (520–570nm wavelength) LED indium gallium nitride (InGaN) semiconductor structures [Yufeng Li et al, Appl. Phys. Lett., vol98, p151102, 2011; reported in Semiconductor Today May/June 2011, p110].

Patterning the sapphire with a hexagonal array of cylindrical holes was found to improve the crystal quality of the nitride semiconductor material through reducing

threading dislocation (TD) densities in the quantum wells of the LEDs where the light is produced. Total internal reflection of light due to the patterning was also reduced, resulting in the enhancement of light extraction efficiency (LEE) by 1.58x.

A number of other groups have developed patterned substrates for improving LED performance. Taiwan's National Chung Hsing University used the air voids created in nitride growth on patterned sapphire to create a method for removing the substrate in a wet chemical etch lift-off process [www.semiconductor-today.com/news_items/2010/SEPT/NCHU_030910.htm].

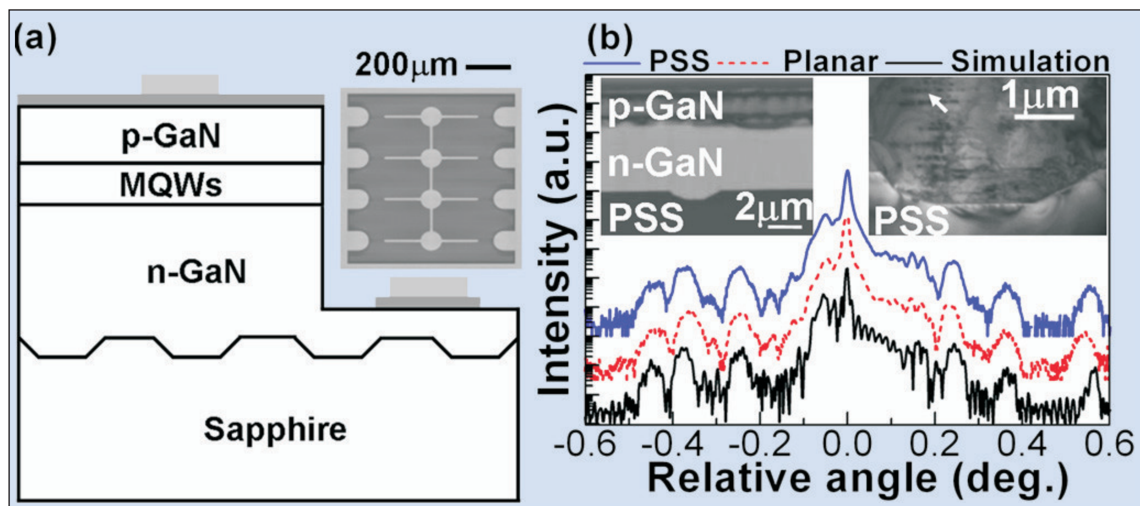

Figure 5. (a) Schematic of the InGaN-based MQW solar cell grown on PSS; inset: SEM image of the actual device. (b) XRD rocking curves of both solar cells; insets: cross-sectional SEM image of the solar cell grown on PSS (left-hand) and an enlarged TEM image focusing on the GaN/sapphire interface (right-hand).

Again in Taiwan, National Central University (NCU) and Academia Sinica used a maskless wet etch to produce pyramid-shaped pits in sapphire to give a 37% increase in light output; meanwhile, National Chiao Tung University researched changes in crystal quality and LED performance brought about by changing the slant angle of pyramids produced with a mask and wet etch process [www.semiconductor-today.com/news_items/2010/ FEB/NCU_100210.htm].

A different example of LED enhancement through patterning is Hong Kong University of Science and Technology and Taiwan National Chiao Tung University developing nano-patterning on silicon rather than sapphire to improve light output by 21% over micro-patterned silicon [www.semiconductor-today.com/news_items/ 2010/MAY/HKU_210510.htm]. The growth of high-quality nitride material on silicon is even more difficult than on sapphire due to a larger lattice mismatch (~17% rather than ~14%).

Solar cell development

Patterned sapphire substrates have also been used to enhance the performance of nitride-semiconductor photovoltaics. National Taiwan Normal University's Institute of Electro-Optical Science and Technology used a PSS to grow nitride semiconductors with more than 70% reduced threading dislocations, resulting in 60% increased short-circuit current in photovoltaic devices processed from the epitaxial material [Ya-Ju Lee et al, Appl. Phys. Lett., vol98, p263504, 2011].

The PSS was produced using a mixture of sulfuric and phosphoric acids to etch the c-plane sapphire substrate at 300ºC. The pattern consisted of triangular {0001} c-plane depressions with side-walls consisting {1-102} r-plane facets. The diameter of the depressions was about 3μm, 0.5μm deep, set at 7μm pitch.

The nitride layers were grown using MOCVD (Figure 5). The light absorption layer consisted of a 10-period multi-quantum well of 2.5nm $In_{0.23}Ga_{0.77}N$ separated by 12nm GaN barriers. Square 800μm x 800μm mesas were etched down to the n-type layer. Indium tin oxide (ITO) was used as a 300nm transparent conducting current-spreading layer on the contact, followed by chromium-gold electrodes. A device was also grown on standard planar sapphire and processed in a similar way.

Examination with scanning electron microscope showed that the GaN grew without air voids, unlike some of the work mentioned above. Cross-sectional transmission electron micrographs show a large number of stacking faults in the trench regions of the PSS that appear to interact with threading dislocations (TDs), preventing their penetration into the MQW region. Molten potassium hydroxide (200ºC) was used to create etch pits that can be counted to give an estimate of dislocation density. For the planar substrate, the TD density was $1.28x10^9/cm^2$; the use of PSS reduced the TD density to $3.62x10^8/cm^2$.

Current–voltage measurements showed a significant reduction of about one order of magnitude (a factor of ten) in reverse bias current in the PSS device, "entirely due to a reduction in leakage paths associated with TD defects in MQW". The respective shunt resistances are estimated at 0.1GΩ and 1GΩ for the PSS and conventional devices, respectively. Operating the PV devices as LEDs gave 30% enhanced electroluminescence for the PSS component due to enhanced light extraction properties. ➤

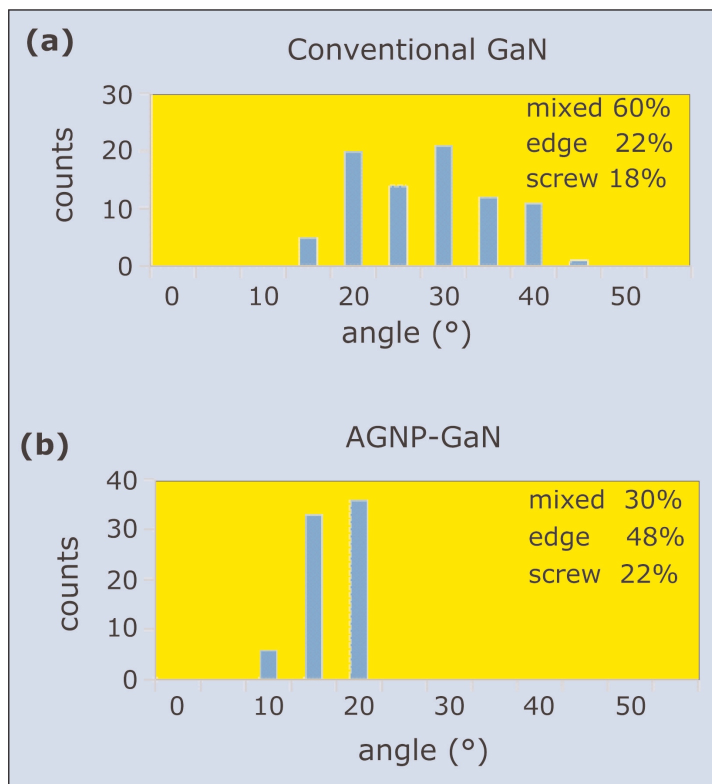

Figure 6. Distribution of dislocation bending angles and types for (a) conventional GaN and (b) AGNP-GaN.

For PV operation under 100mW/cm^2 1.5AM light, the open-circuit voltage of 2.05V was the same for both devices. However, the short-circuit current density was enhanced by 60% at 1.09mA/cm^2 for the PSS device, compared with 0.68mA/cm^2 for the conventional cell. The maximum power densities were 1.14mW/cm^2 (PSS) and 0.79mW/cm^2 (planar). However, the fill-factor was reduced from 57% (0.79/2.05x0.68) to 51% (1.14/2.05x1.09) for the conventional and PSS devices, respectively.

Earlier this year, another group of Taiwan-based researchers at National Cheng Kung University, National Chiao Tung University, and Southern Taiwan University also used epitaxy on PSS to improve the performance of nitride semiconductor solar cells [C.C. Yang et al, IEEE Electron Device Letters, published online 24 February 2011; reported ST April/May 2011 p76]. These patterned substrates had truncated cone structures created using photolithography and etch. The conversion efficiency of the patterned device was 1.71%, compared with 1.34% for the cell grown on planar sapphire. A conversion efficiency of 2.95% for nitride-based PV cells was achieved by Texas Tech University researchers last year (www.semiconductor-today.com/news_items/2010/AUG/TEXAS_240810.htm).

Characterization and tools

Lehigh University researchers in the USA have tried to look more closely at what goes on when GaN is grown on patterned sapphire [Wanjun Cao et al, J. Appl. Phys., vol110, p053505 p2011]. The researchers compared GaN quality resulting from a conventional GaN-on-sapphire method with an 'abbreviated growth mode' on nano-patterned c-plane sapphire (AGNP-GaN).

The conventional growth consisted of 30nm low-temperature (535ºC) GaN buffer, hydrogen etch-back, and high-temperature (1080ºC) GaN recovery and growth.

The nano-patterned sapphire substrate was created through a process of oxidation and epitaxial conversion of aluminum islands developed at Lehigh. This process results in a square array of 200–300nm diameter bumps with a pitch of about 1000nm. The square array of aluminum mesas was defined through electron-beam lithography. The height of the resulting Al_2O_3 bumps was about 100nm.

The AGNP-GaN growth consisted of a 15nm LT-GaN buffer and immediate HT-GaN deposition without etch-back/recovery.

The island growth phase created non-uniform, irregular features with conventional planar substrate; but in AGNP-GaN growth the islands had greater regularity in spacing, size and geometry, being located preferentially in the valleys between the sapphire bumps. Further, the AGNP-GaN islands had distinct inclined facets that have been associated with dislocation bending during coalescence. Dislocation bending is thought to be a major source of dislocation reduction in GaN.

Coalescence occurred after about 12 minutes of HT-GaN growth on the AGNP-GaN islands, giving a layer of 0.25μm. The conventional growth layer coalesced after 22 minutes with 0.66μm thickness.

While dislocation densities reduced five-fold between 2μm and 3.5μm thickness on conventional sapphire, the most dramatic reductions in dislocation density for AGNP-GaN occurred before 0.5μm. In the conventional GaN, dislocation bending occurred about 2.5μm, while in AGNP-GaN it is seen to occur before 1μm. After 4μm, the dislocation density in both types of material is estimated to be about 5x10^8/cm^2. Dislocations included mixed, edge and screw types (Figure 6).

The researchers conclude: "These findings support earlier results showing that InGaN QW LEDs grown on nano-patterned sapphire showed enhanced output power and carrier lifetime compared with those grown on a planar template. The indication also is that AGNP-GaN may achieve equivalent or better performance than conventional GaN at much smaller thickness, saving time and expense in growth."

A number of companies are responding to the increased interest in patterned sapphire with tools such as atomic force microscopes (AFM, e.g. Bruker), wafer scribes (e.g. ESI), nanolithography (e.g. Eulitha) and automated defect inspection (e.g. KLA–Tencor). ■

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