

Seeking to unlock wide-range potential of nitride photovoltaics

Up to now, nitride semiconductor solar cells have only responded to the high-energy, short-wavelength end of the solar spectrum. Mike Cooke reports on recent attempts to extend this range.

Nitride semiconductors have remarkable properties in terms of light emission, and it is hoped that in the next few years highly reliable and efficient lighting based on the technology will extend from niche applications into street and general applications, reducing world energy consumption and carbon dioxide emissions. But could nitrides do more and actually provide significant energy from sunlight?

In theory, gallium indium nitride (GaInN) semiconductors should be able to cover the greater part of the range of solar photons (Figure 1). Although adding in aluminum to make AlGaIn could extend this slightly to 200nm (6.2eV) deep-ultraviolet wavelengths, this is not really the direction needed to convert more sunlight at ground level. However, mixed with indium, aluminum (AlGaInN) could provide useful layers in terms of alternative lattice constants.

The potential of the GaInN system allows one to envisage a series of different nitride solar cells designed to extract most efficiently a range of different wavelengths. Even for single cells, one could tune a photovoltaic cell that could achieve better than 50% solar energy conversion by using InGaIn alloy with an indium fraction of 40%. Using triple junctions of nitride material pushes this to almost 60% conversion; a four-junction nitride device has an estimated conversion efficiency of 62%. Of course, all these figures are based on simulations using non-existent ideal materials.

It is envisaged that these devices would be used in concentrator photovoltaic (CPV) systems where optical systems are used to focus the incoming solar radiation on small-area nitride PV chips, lowering costs. Further potential advantages of nitride solar cells are radiation hardness, high thermal conductivity, and high light absorption. These features would enable deployment in harsh environments such as space and deserts.

Unfortunately these remain theoretical hopes because it is very difficult to grow high-quality InGaIn with high

indium contents (>20%). The problem is that the lattice mismatch between InN and GaN is high (~11%). Layers with appreciable indium contents tend to segregate into regions with high and low indium content (phase separation). This is one of the difficulties that have hindered the extension of nitride light-emitting technology to longer wavelengths (e.g. green laser diodes, yellow LEDs).

Despite the difficulties, university groups across the world are developing nitride semiconductors for use in solar cells. Although much of the research in this direction is focused on producing better-quality high-indium-content GaInN or even InN, some groups have produced actual solar cells. These are usually based on established nitride semiconductor technology that has already successfully resulted in light-emitting and laser diodes. Hence the range of wavelengths is restricted to those shorter than green (~530nm), and usually even shorter (violet, ~410nm).

Working up from InN

In Europe, the 'RAINBOW' collaboration [<http://rainbow.ensicaen.fr/>] is seeking to develop high-quality InN and In-rich nitride alloys. The collaboration consists of 13 groups from eight countries. Solar cells are among the targets for these efforts. Recent work coming from one of these institutions includes Universidad Politécnica de Madrid, along with Paul-Drude-Institut für Festkörperelektronik, developing InN/InGaIn multiple quantum wells that emit at the infrared 1.5µm wavelength under 14K photoluminescence [J. Grandal et al, Appl. Phys. Lett., vol98, p061901, 2011].

In the UK, University of Warwick researcher Dr Tim Veal is the principal investigator for the 'Nitride Photovoltaic Materials for Full Spectrum Utilization' project funded by the UK Engineering and Physical Sciences Research Council (EPSRC). The £694,057 (~\$1m) project began in 2008 and is expected to continue to 2013. The project partners will supply samples; the

collaborators are mainly outside the UK: Caen University (France), Cornell University (USA), University of Canterbury (New Zealand), and Sharp Laboratories of Europe Ltd (based in UK). Warwick is also involved in RAINBOW.

The ESPRC project promises that "a comprehensive program of structural, optical and electrical characterization will be undertaken to optimize these alloys for application in nitride-based photovoltaic devices. In parallel with these activities,

experiments will also be undertaken on III-nitride structures to achieve reproducible n- and p-type doping, to develop tunnel junctions, to determine the role of defects in photovoltaic performance, and to optimize metal contacts and transparent conducting oxide (TCO) solar cell windows. Solar cell modeling will be performed using material parameters determined from the experiments to produce optimized designs for high-efficiency nitride solar cells and to investigate new integrated optical/electrical solar cell designs which circumvent traditional current and lattice matching constraints."

Veal comments on progress so far: "Our largest contribution has been to discover the electron accumulation at the surface of InN as opposed to the depletion layer that exists at almost all other semiconductor surfaces. This has implications for contacts (they will be Ohmic rather than Schottky) and in a PV context means that tunnel junctions could be rather difficult to make. We have also studied the change from accumulation to depletion as Ga is added to InGaN alloys.

"Another major consequence of the electron accumulation is that p-type InN (produced by Mg-doping, as with commercial GaN-based devices) does not appear to be p-type from Hall-effect measurements because the surface electron-rich layer dominates these measurements and the 'buried holes' are 'hidden' underneath — when the material is p-type, an inversion layer exists whereby the material is n-type at the surface and p-type beneath.

"We have also investigated p-type doping of InN and both InGaN and InAlN alloys. We have found that p-type doping is possible for all InGaN compositions and all but the most Al-rich InAlN alloys. Obviously, p-type doping is vital for making p-n junctions which are the basis of solar cells."

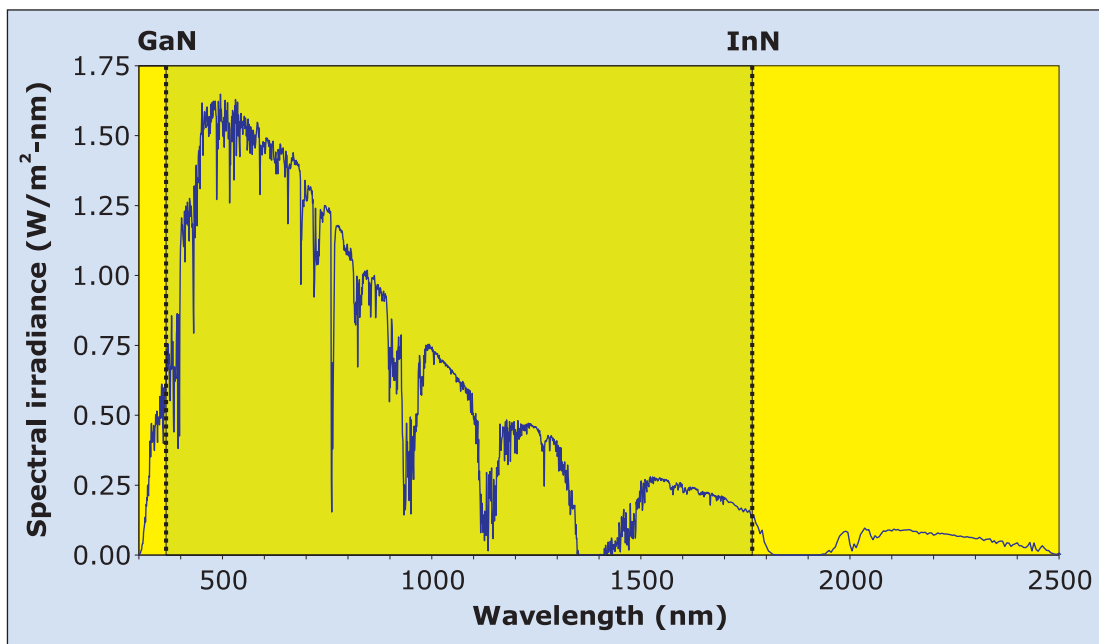


Figure 1. ASTM G173-03 AM1.5G — air mass 1.5 — reference spectrum, representing 'normal' solar light characteristics at the earth's surface at mid latitudes i.e. solar zenith $\sim 48^\circ$, seen as a rough average for conditions in US, Europe and Japan.

Taiwan's National Tsing-Hua University and National Synchrotron Radiation Research Center (NSRRC) have recently been able to avoid electron accumulation in InN by reversing the polarity from (0001)/In-face to (000 $\bar{1}$)/N-face [Appl. Phys. Lett., vol98, p052101, 2011]. A surface treatment is used to remove any In adlayer at the (000 $\bar{1}$) surface.

Tsing-Hua Professor Shangjr (Felix) Gwo, a leader of this research, comments: "For growing high-quality InN samples, nitrogen-plasma-assisted MBE is preferred because of the necessity of low growth temperature (less than 550°C). Additionally, crystal polarity control of III-nitrides by MBE growth can be achieved, in contrast to the conventional MOCVD method.

"For example, for the growth of N-polar InN(000 $\bar{1}$), we can use a crystalline Si₃N₄ buffer layer formed on the Si(111) substrate by nitrogen-plasma nitridation as the growth template. Alternatively, we can also grow both N-polar InN(000 $\bar{1}$) and In-polar InN(0001) on sapphire substrates under suitable MBE growth conditions.

"The implication of our work is that the surface electron accumulation phenomenon is not really 'universal', as claimed by previous studies. Nor is it a real barrier to prevent the realization of p-type doping for high-indium-content InGaN alloys."

Veal's group in Warwick reports that it has also been able to reduce electron accumulation by increasing magnesium (Mg) doping, altering the surface Fermi level in work yet to be published. The researchers think that this is correlated with the amount of surface In-adlayers, since In-In bonding is thought to be a cause of surface donors contributing to electron accumulation. ▶

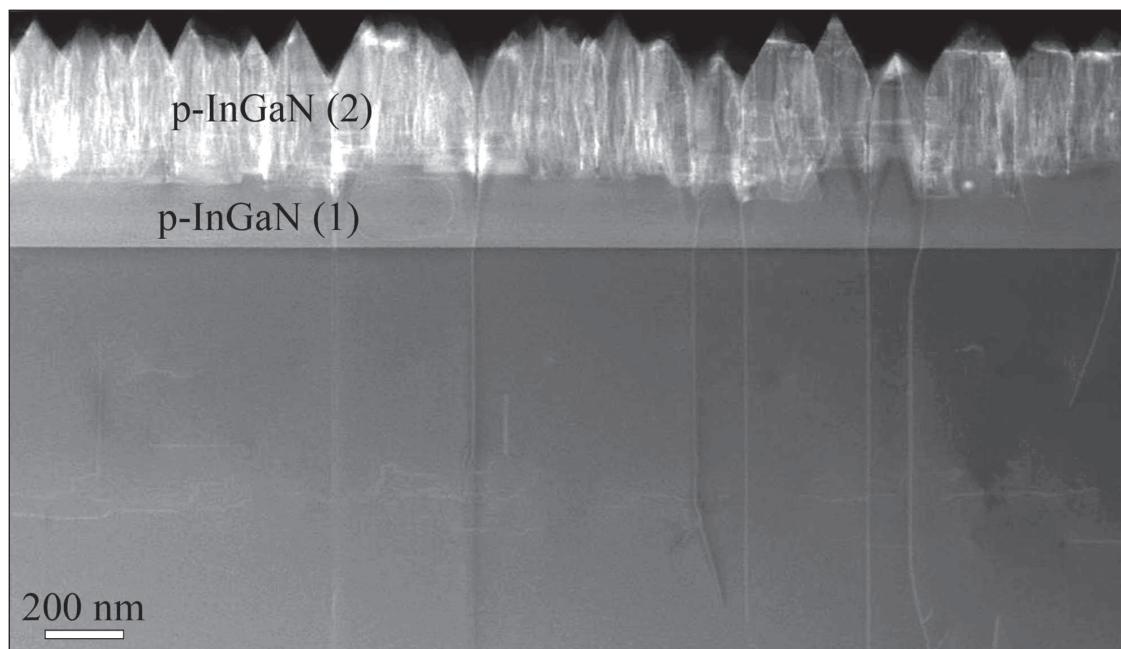


Figure 2. Scanning transmission electron micrograph (STEM) from Japan at National Institute for Materials Science of p-InGaN sample, which shows two obvious regions with different dislocation densities.

► Veal comments: "Our observed reduction of the electron accumulation with increasing Mg doping is rather convenient as it will help in the effort to make tunnel junctions for current collection in the In-rich part of a multijunction solar cell — something that was previously thought to be hampered by electron accumulation."

Further characteristics of Mg doping, in producing p-InGaN alloy, has been the subject of investigations at Japan's National Institute for Materials Science (NIMS) [Liwen Sang et al, *Appl. Phys. Express*, vol3, p111004, 2010]. In normal p-GaN, the Mg acceptor activation energy is quite high, meaning that the density of holes that results is usually lower than that achieved for electrons by silicon-doped n-GaN layers. This imbalance in the ability to produce nitride semiconductor p-n junctions has been a source of difficulty for high-efficiency light-emitting and absorbing devices.

One attraction of Mg-doped InGaN alloy is that the activation energy is smaller than for pure GaN. However, the NIMS researchers found that, although hole density is increased in p-InGaN relative to p-GaN, the material tends to separate into two layers (Figure 2). X-ray diffraction analysis reveals that the first layer is compressively strained to match with the GaN substrate, while the second is relaxed by generating threading dislocations. There was no phase separation observed in an InGaN layer produced under similar conditions but without the Mg doping. The undoped GaN had an In content around 8%. In one of the doped samples, the In content of the strained layers was 6.9%, while the dislocated relaxed layer had an In content of 11.2%.

Solar cell achievements

US company RoseStreet Energy Labs Inc is one company working on producing nitride semiconductor solar cells.

The company has close links with the US Lawrence Berkeley National Laboratory (LBNL), with chief technology officer Dr Wladek Walukiewicz working for both organizations.

LBNL, with RoseStreet and Sumika Electronic Materials, has published a potential way to produce multi-band solar cells without multi-junctions [N. López et al, *Phys. Rev. Lett.*, vol106,

p028701, 2011]. Rather than alloying the III-side of the III-V equation, LBNL et al mix nitrogen and arsenic from the group V side, keeping the group III material constant (Ga). The resulting GaAsN material has both a wide and 'intermediate' bandgap that allows for sensitivity to three bands of solar energy (Figure 3). This enabled the researchers to produce 'proof of concept' cells with sensitivity over a wide range of the solar spectrum.

LBNL has been working on the technology of nitride solar cells for some time, producing multi-junction solar cells in 2002. In 2004, researchers at LBNL developed the intermediate-band concept, using zinc manganese telluride (ZnMnTe) doped with oxygen to create the intermediate band. Walukiewicz says of this older process that manufacturing the ZnMnTe alloy is complex and time-consuming, and these solar cells are also expensive to produce in quantity.

The new GaAsN material can be produced using MOCVD. In fact, the nitrogen component is dilute (2.4% nitrogen), so the material is close in structure to the gallium arsenide (GaAs) substrate (heavily doped n-type). The nitrogen atoms substitute for some of the arsenic, producing the intermediate band. The material was designed using LBNL's 'band anticrossing model' that has been developed at the facility for the past ten years. The model suggested that around 2% nitrogen could provide the right sort of material for solar cells.

Kin Man Yu, a collaborator with Walukiewicz since the work in 2002, comments: "We knew where the intermediate band ought to be and what to expect. The challenge was designing the actual device." ►

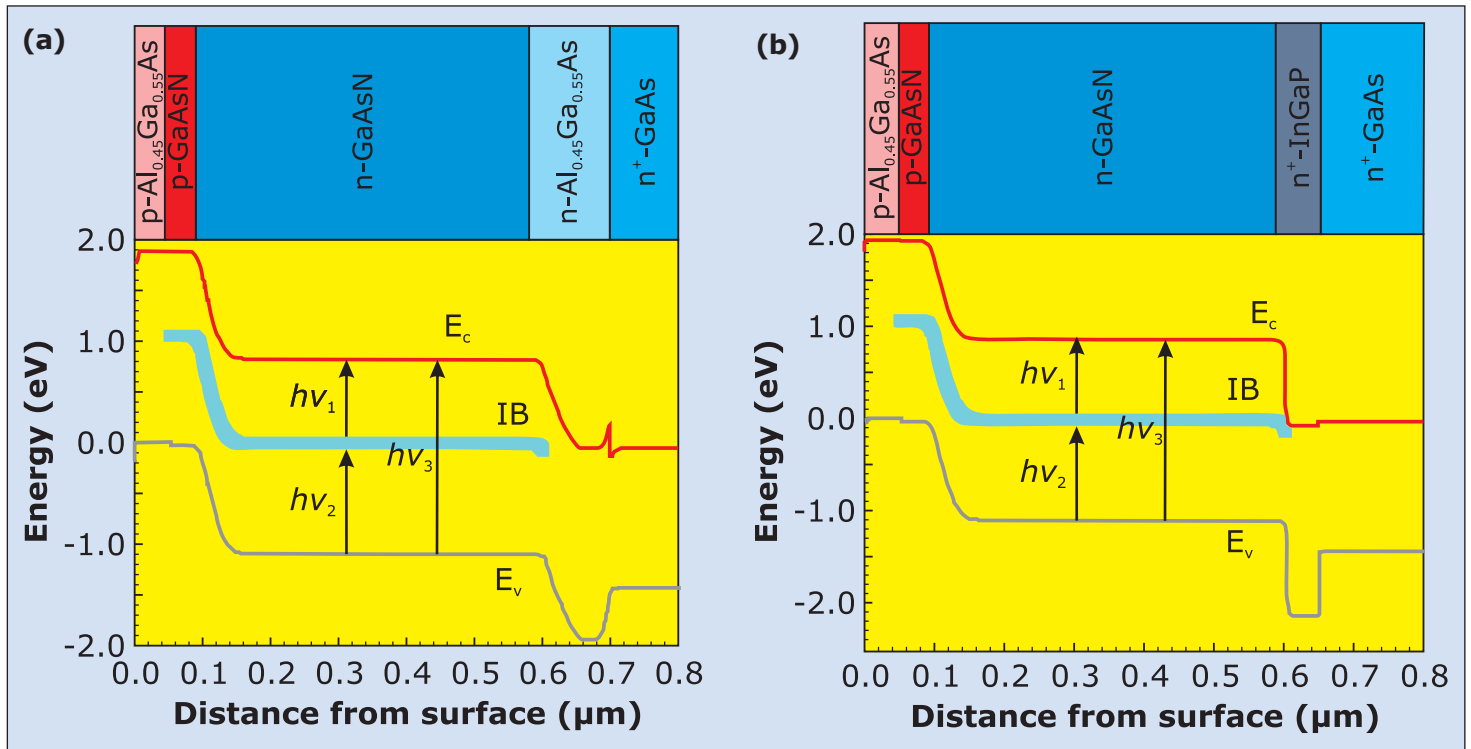


Figure 3. LBNL et al intermediate-band solar cell device structures and band diagrams: (a) shows a device with intermediate band blocked from conducting to the contacts; (b) an unblocked structure.

► Part of the design was aimed at blocking leakage from the intermediate band (Figure 3). The resulting device responded 'strongly' (Figure 4) to all parts of the solar spectrum (1.1–3.2eV). Comparison tests of the device and material included creating devices with unblocked intermediate band, and producing LEDs from the epitaxial structure.

The open-circuit voltage of the blocked intermediate-band structure was 0.92V, while that of the unblocked comparison device was 0.42V. When one compares

these results with the values expected from the full bandgap (2eV) and intermediate gap (1.1eV), there is clearly a large offset in both cases. The offset depends on the material and junction quality, along with the sun concentration factor. The researchers comment on the offset: "The large value of the offset found in both cases is most likely related to a short minority carrier lifetime, as has been previously found in GaInNAs alloys."

University of California Santa Barbara (UCSB) has a

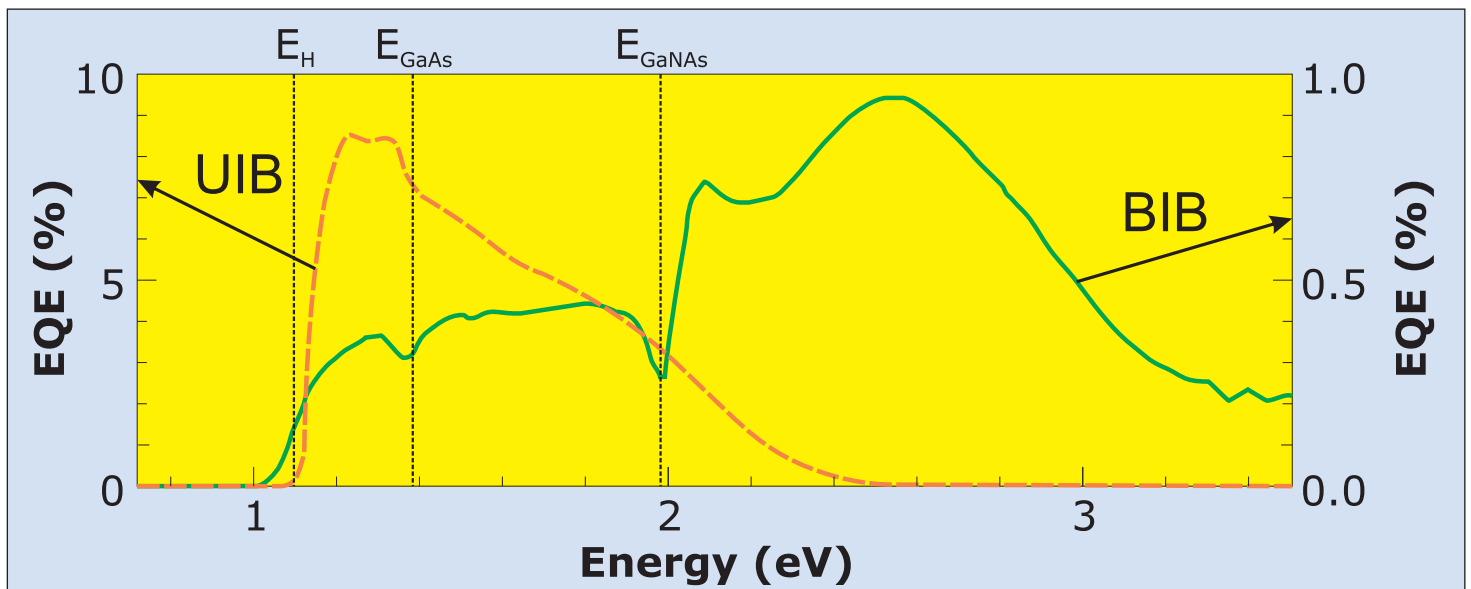


Figure 4. Spectral dependence of external quantum efficiency of LBNL et al intermediate-band solar cell. Solid line represents device with blocked intermediate band (BIB) and dashed line corresponds to cell with unblocked intermediate band (UIB).

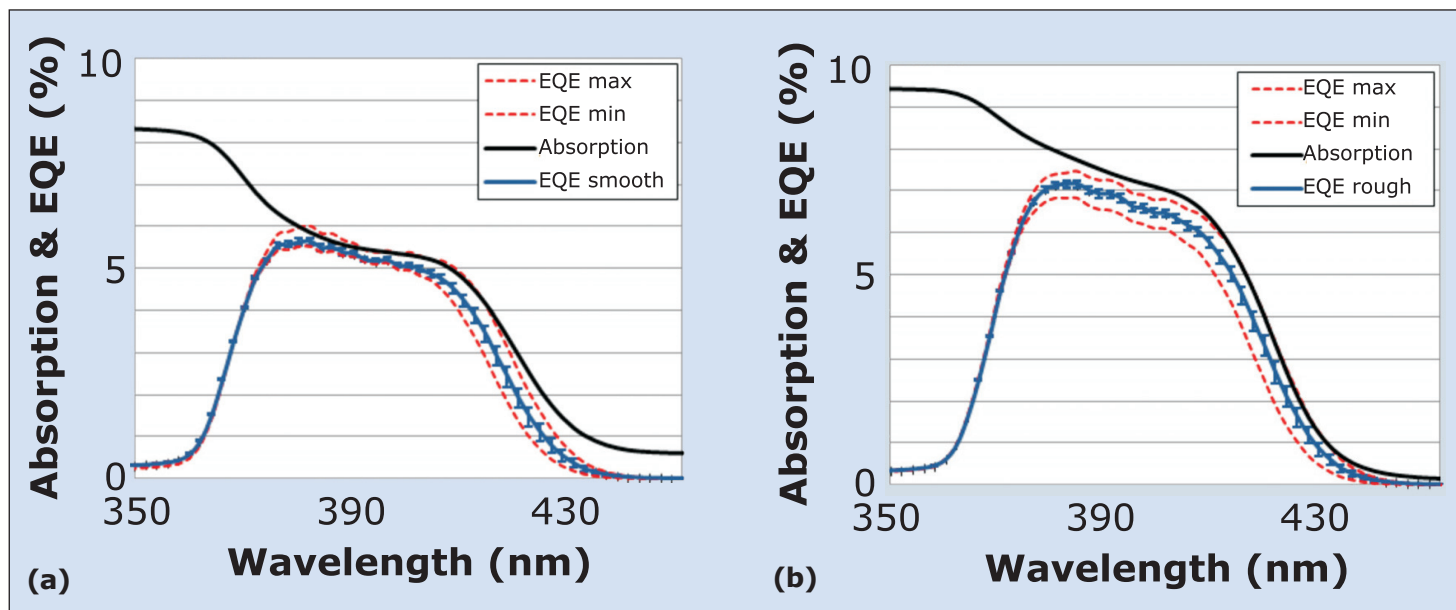


Figure 5. UCSB measured absorption (solid), average (solid with error bars), maximum and minimum (dashed curves) EQE curves for (a) smoother and (b) rough samples. The average EQE and its standard deviation (error bars) were determined from measurements of a total of 12 devices located in the same area of the sample where the absorption was measured.

strong team of nitride semiconductor researchers, including Shuji Nakamura, a pioneer of the field. This year, UCSB has reported nitride semiconductor photovoltaic devices with external quantum efficiencies (EQE) up to 72% [Elison Matioli et al, Appl. Phys. Lett., vol98, p021102, 2011]. One of the researchers, Claude Weisbuch, is also associated with Ecole Polytechnique in France.

Much of the nitride semiconductor work at UCSB concerns light-emitting devices. However, some of the same researchers have previously reported (2008) photovoltaic (PV) devices that achieved up to 63% external quantum efficiency. Although these EQEs are impressive, one has to bear in mind that these devices cover only a small range in a not particularly useful part of the solar spectrum.

In both the latest and 2008 work, UCSB used InGaN active layers with 12% In content. This restricts the effective performance of the devices to the wavelength

range 370–410nm, a tiny sliver of the AM1.5G illumination spectrum (Figure 1). The short-wavelength limit is determined by the bandgap of the p-GaN contact layer and the long-wavelength limit by the active layer bandgap.

In the latest devices, the undoped InGaN active layer was sandwiched between p- and n-GaN layers with high levels of doping ([Si] ~ 6x10¹⁸/cm³, [Mg] ~ 8x10¹⁹/cm³). The high doping was intended to counteract the effects of polarization fields that normally degrade photovoltaic performance in nitride semiconductors. Surface roughening was used to increase the coupling of light into the device. The devices were grown on sapphire using MOCVD.

The EQE follows the absorption curve closely in shape and magnitude (Figure 5) in the InGaN absorption region of (370–410nm). “This means that nearly all absorbed photons in this layer were converted into electrons and holes, and these charges were efficiently separated and transported out of the device,” the researchers comment. Further performance measurements were carried out to determine the standard performance metrics (Table 1).

Meijo and Nagoya universities in Japan have also recently extended previous work on nitride semiconductor solar cells, improving performance through superlattice structures [Yousuke Kuwahara et al, Appl. Phys. Express, vol4, p021001, 2011].

One problem in using GaInN for active layers in solar cells is that misfit dislocations tend to form in thick layers. When a Ga_{0.8}In_{0.2}N layer is put on GaN the critical thickness is of the order 1nm, and the resulting dislocations lead to pits at interfaces that degrade

Table 1. Solar cell performance metrics: open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill-factor (FF = P_{max}/V_{oc}xJ_{sc}), and peak EQE.

Device	V _{oc} V	J _{sc} mA/cm ²	FF %	EQE _{peak} %
UCSB smooth	1.83	0.83	76.6	56
UCSB rough	1.89	1.06	78.6	72
Miejo/Nagoya A	1.83	0.37	50.6	3.5
Miejo/Nagoya B	0.93	3.19	53.3	46.1
Miejo/Nagoya C	1.78	3.08	70.8	59.1

solar cell performance. However, thicker layers are needed to absorb sufficient sunlight.

The Meijo/Nagoya researchers produced devices using a number of thin layers (superlattices) to overcome this problem. The researchers comment: "This is the first time that thick GaInN-based superlattices have been used as an active layer in solar cells to the best of our knowledge."

Previous work by the Meijo/Nagoya group includes using free-standing gallium nitride (GaN) substrates. In that work, the conversion efficiency was 1.41%. This has now been increased to 2.5% for standard AM1.5G illumination. Again, the type of device used covers only a tiny part of the solar spectrum, so the 2.5% conversion efficiency figure is considered high for present nitride-based solar devices. The maximum external quantum efficiency was 59.1% for the best device.

Three devices were produced (Figure 6) with various combinations of superlattice. Sample C was created to combine the good features (Table 1) of the earlier devices, reducing dislocation densities and thus improving the material quality of the subsequently grown material, leading to a device with high EQE and internal quantum efficiency estimated at 88% at 390nm (violet).

Last year, Texas Tech University scientists reported an indium gallium nitride (InGaN) solar cell with characteristics 'significantly higher' than previously reported values for devices with similar In-content in the QWs (~35%) [R. Dahal et al, Appl. Phys. Lett., vol97, p073115, 2010; reported in Semiconductor Today, September 2010, p82].

The Texas researchers used a 12-period multi-quantum well (MQW) structure consisting of InGaN/GaN (3nm/16nm) with the indium content of the well targeted at 35%. The wavelength of the electroluminescence from the structure was around 533nm (green). Standard AM1.5 characteristics were: open-circuit voltage 1.8V, close-circuit current density 2.56mA/cm², maximum power 2.95mW/cm². This gives a fill-factor of 64% (2.95/1.8/2.56).

The conversion power efficiency of 2.95% falls short of the ~8% theoretical maximum for the frequency characteristics of the device. The improvement was attributed to improved InGaN material quality.

One of the reasons for the still too low efficiency was the small thickness of the well regions (12x3nm =

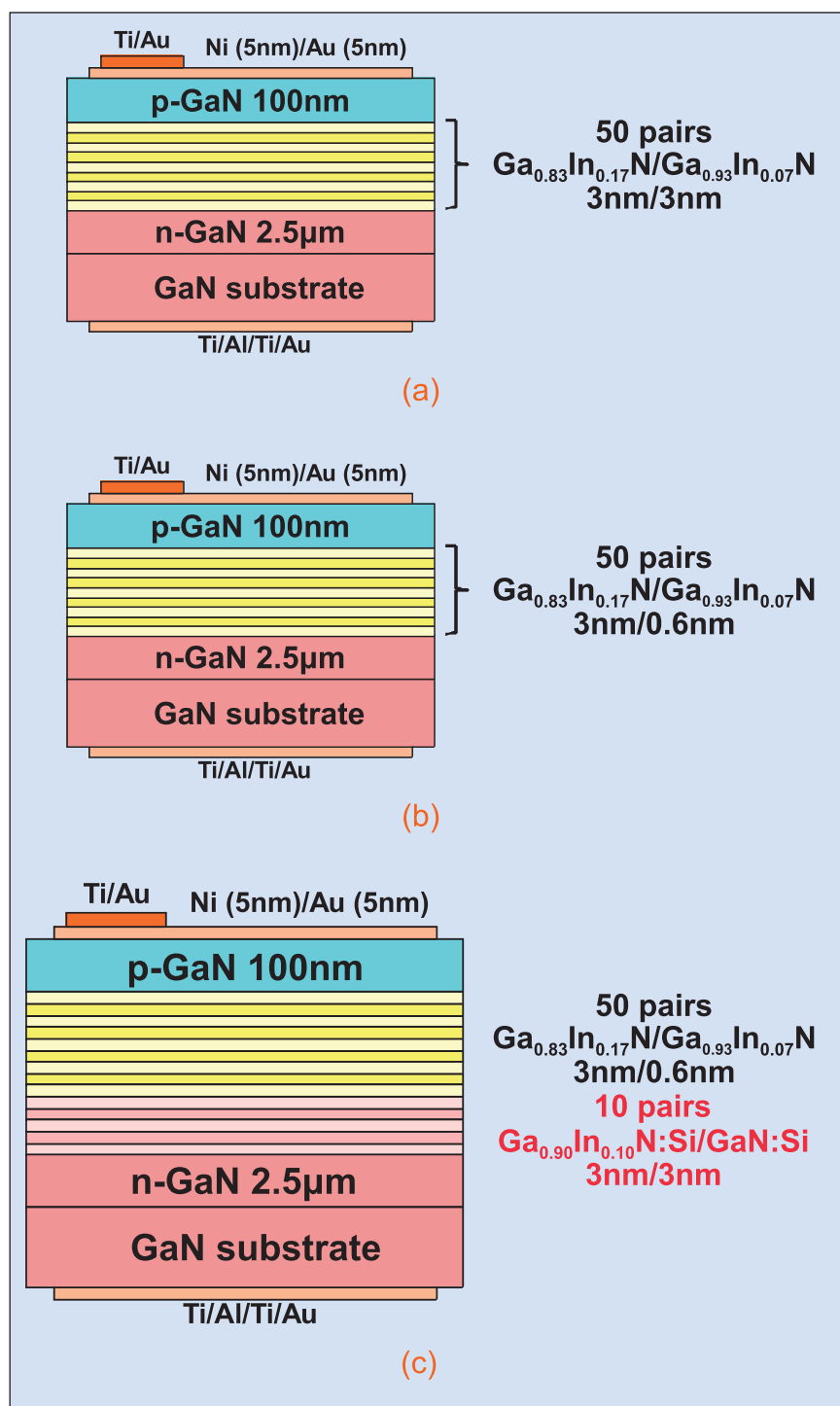


Figure 6. Schematic view of sample structures. (a) Sample A: GaInN-based solar cell with 50 well/barrier layer pairs of $\text{Ga}_{0.83}\text{In}_{0.17}\text{N}$ (3nm)/ $\text{Ga}_{0.93}\text{In}_{0.07}\text{N}$ (3nm) as superlattice active layer. (b) Sample B: GaInN-based solar cell with 50 pairs of $\text{Ga}_{0.83}\text{In}_{0.17}\text{N}$ (3nm)/ $\text{Ga}_{0.93}\text{In}_{0.07}\text{N}$ (0.6nm). (c) Sample C: Sample B with 10 additional well/barrier pairs of $\text{Ga}_{0.90}\text{In}_{0.10}\text{N}:\text{Si}$ (3nm)/ $\text{GaN}:\text{Si}$ (3nm) ([Si] doping concentration in both cases is $3 \times 10^{18} \text{ cm}^{-3}$).

36nm). Complete light absorption would require at least 200nm. Evidence for this came from comparing devices with and without back-reflector. The reflector added 15% to the photocurrent density by effectively doubling the thickness of the well region. ■