Progressing etch techniques for compound semiconductors

Mike Cooke reports on some recent developments in using various etch processes on compound semiconductors.

It is often surprising to the newcomer to compound semiconductor production how little etch figures in the description of device construction. The focus tends to be on improved crystal growing and epitaxial layer growth. Etch only appears late on in the production process to create gross structures such as ridges for laser microcavities, mesas and waveguides, along with the creation of contact areas and wiring.

Here we look at developments over the past year where etch is used in a non-standard format. We also consider one area where an etching action occurs where one would prefer it didn't.

Selective boost to nitride light emission

Zhilai Fang at Xiamen University in China has been exploring the use of etch techniques to improve nitride light emission [1]. The aim was to reduce the negative effects of threading dislocations and indium-rich clusters in indium gallium nitride (InGaN) layers. However, one has also to recognize that the light-emission processes in InGaN are not properly understood.

The consensus is that light emission is actually enhanced by a variety of imperfections leading to nano-scale indium content fluctuations, creating localized energy states. Among these imperfections are: spinodal decomposition in which components separate into regions with different chemical and physical properties; phase separation; and, the tendency of indium to aggregate. At too high indium concentration, surface pitting occurs, reducing crystallinity and therefore hitting quantum efficiency of light-emitting structures.

Some recent studies suggest another explanation in terms of inhomogeneous strain effects. These effects can influence the growth modes of the layers (islands that coalesce or complete layers) and can create anomalous light-emission effects.

To study some of these questions, Fang intentionally etched threading dislocation (TD) sites using an in-situ selective process. Fang attributes increased light emission resulting from this process to the suppression of non-radiative recombination near the TD sites.

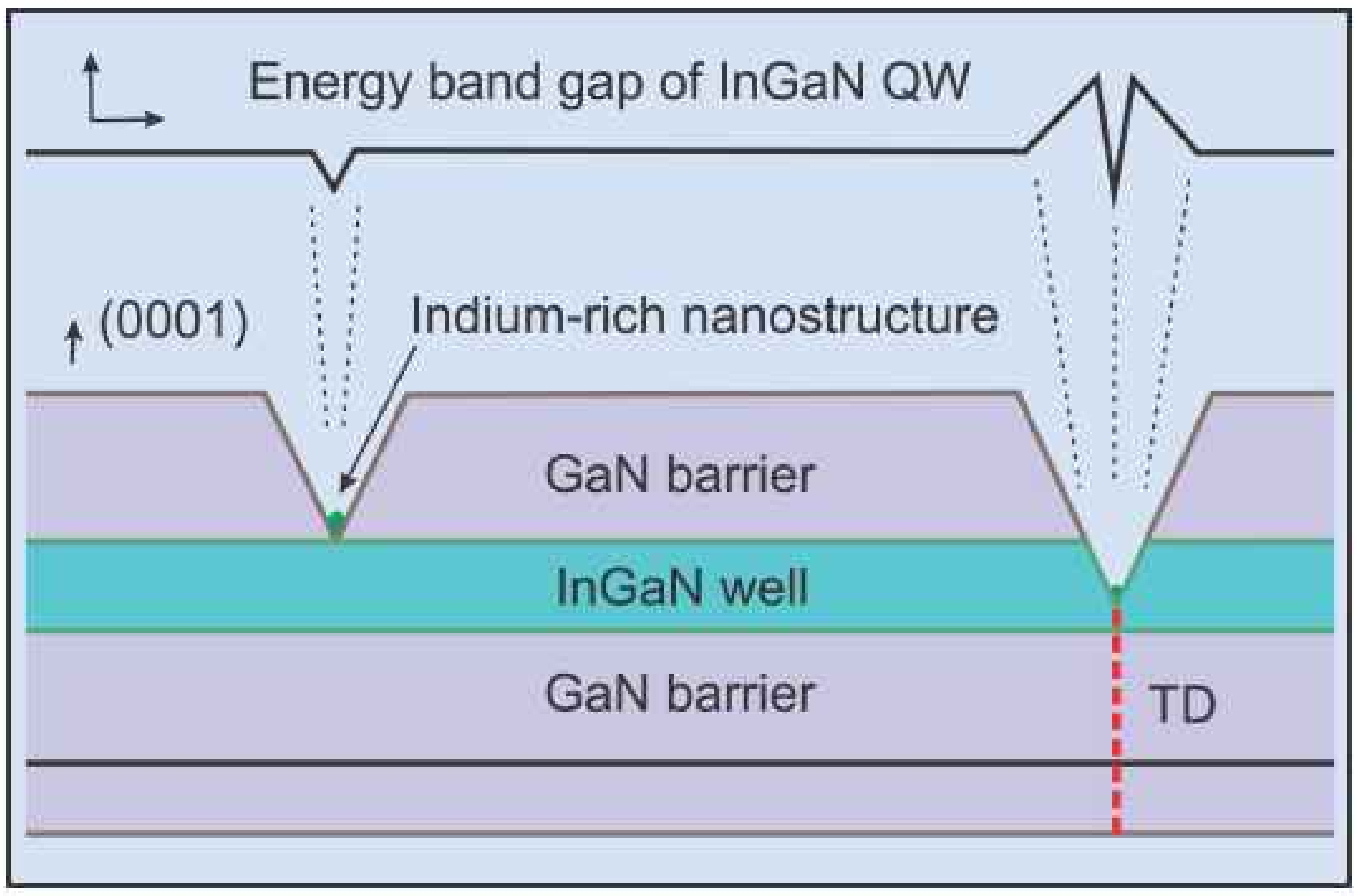

Figure 1. Schematic for the formation of V-shaped pits and the effect on the energy bandgap of the InGaN active layers around the threading dislocations.

Fang grew his InGaN layers using metal-organic chemical vapor deposition (MOCVD) on c-sapphire substrates, using tri-methyl gallium (TMGa), tri-methyl indium (TMIn) and ammonia (NH_3) as precursors. Silane (SiH_4) was used as n-type dopant. GaN nucleation and buffer layers were grown using traditional methods. This was followed by a surface treatment using a droplet homoepitaxy technique developed by Fang and his colleagues to improve the surface/interface with subsequent layers, enhancing the quantum well properties. Ga droplets deposited in this process are designed to serve as both nuclei for subsequent growth and as a surfactant. The resulting layers have been found to have increased photoluminescence (PL), and can be arranged to have narrower line-width [2].

The InGaN/GaN interface was treated with indium by varying the TMIn flow rate for a few seconds. An ultrathin GaN layer was used to protect the well (WPL = well protection layer) from indium losses during thermal processes and for strain pre-relaxation to improve surface smoothness. The indium treatment results in In-rich nanostructures and V-shaped pits. The treatment resulted in some improvement in surface

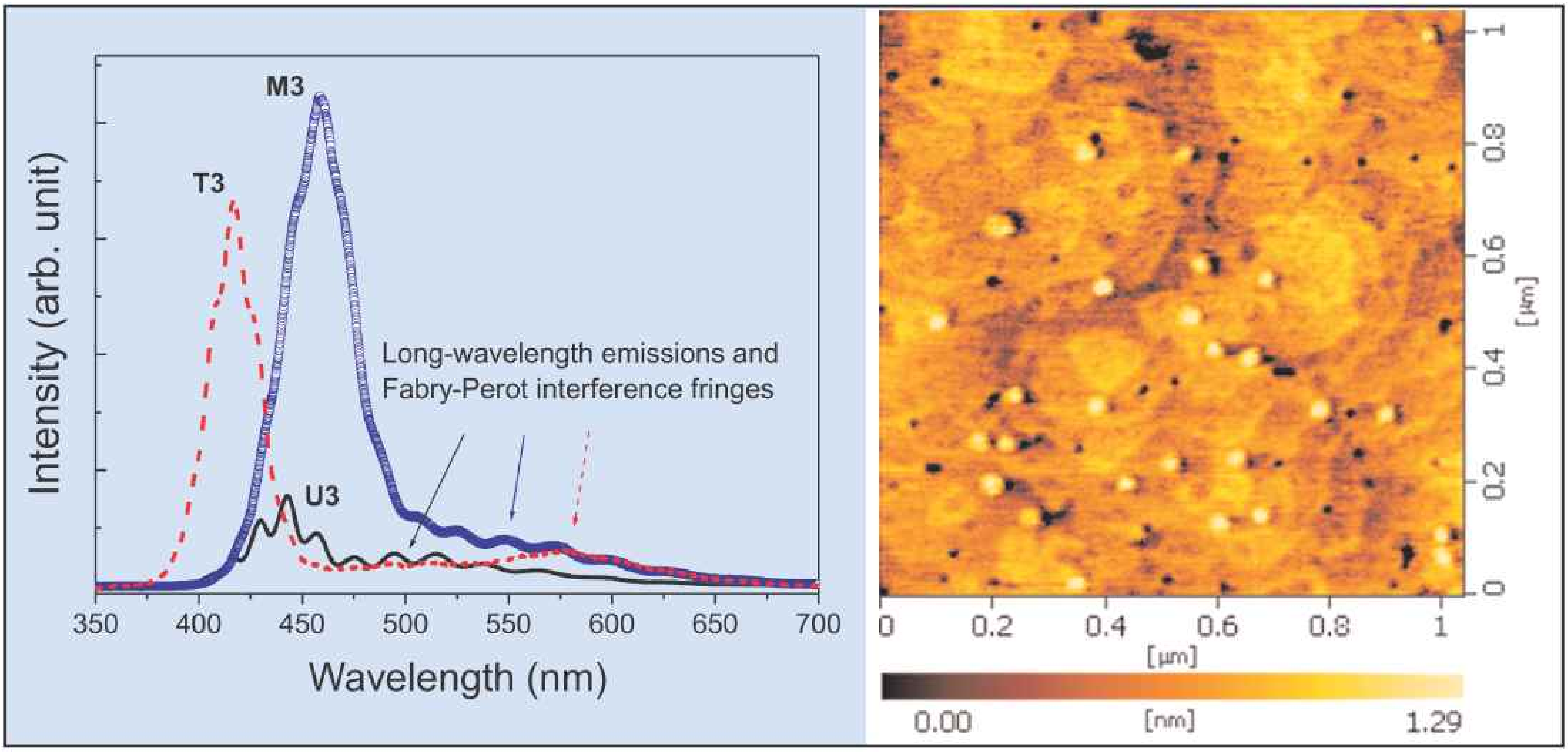

Figure 2. Photoluminescence spectra at 300K for untreated (U3) and treated (T3) quantum wells, and a modified treatment (M3) to reduce phase separation effects. The long-wavelength tail shows emissions from In-rich nanostructures and interference fringes from Fabry–Perot reflections. Also shown is the surface morphology of bare InGaN epilayers with a moderate indium post-treatment using a TMIn flow rate of 40sccm (M1), as revealed by atomic force microscopy.

smoothness: the root-mean-square (RMS) roughness was 0.5nm for untreated samples, but was reduced to 0.4nm in treated samples.

Fang believes that some of the V-shaped pits are the result of selective etching of TDs by the indium flow where the screw and mixed dislocations in such regions become chemically active (Figure 1). Other pits may result from In-rich nanostructures that form on the well during the subsequent GaN barrier growth. The size of typical pits was around 20nm, with a depth of 0.7nm. The density of pits was around $4x10^9/cm^2$. Since the etching of these pits removed some active InGaN material around TDs, it was expected that a potential barrier would be raised to electrons and holes, increasing the bandgap.

Photoluminescence characterization (Figure 2) revealed a double peak that Fang attributes to the separate emissions from the quantum well (QW) and In-rich nanostructures. The spectra also reveal Fabry–Perot interference fringes from interface reflections, indicating the smoothness of the surfaces. The QW peak for the untreated sample (U3) was 442nm, while the longer-wavelength peak from the nanostructures was around 510nm. For the treated sample (T3), the peaks were 417nm and 574nm, respectively. The treatment therefore blue-shifts QW emissions while red-shifting nanostructure peaks (from green to yellow). U3 had a nanostructure/QW peak intensity ratio of 0.38, while for T3 this was reduced to 0.09. The QW emission for T3 was approximately four times that for U3.

The large blue-shift of the T3 QW peak suggests phase-separation effects from the strong indium treatment. Fang therefore tried a modified TMIn flow of 40 cubic centimeter per minute at standard temperature and pressure (sccm), instead of the original 160sccm. The QW peak was then 459nm and the long wavelength was 537nm, indicating successful suppression of phase separation.

Although the Xiamen University group has presently only applied these techniques to undoped structures in photoluminescence studies, Fang believes that the technique should also apply for electroluminescence measurements with appropriate doping to achieve p-GaN and n-GaN layers for diode action.

Light-enhanced wet etch eats into nitrides

Researchers based in Crete, Greece, have been developing photo-enhanced wet etch techniques for use with nitride-based semiconductors. Illumination with ultraviolet light of a well-defined wavelength enables selection of some III-nitride materials and not others to etch into with an electrochemical solution of potassium hydroxide (KOH) in water.

Normally, group III-nitrides such as GaN are highly resistant to wet chemical etching methods therefore plasma techniques have to be used. However, plasma processing tends to leave ion-induced damage and rough sidewalls in its wake. For optoelectronic devices, such as lasers, smooth sidewalls for cavities can be extremely important.

➤

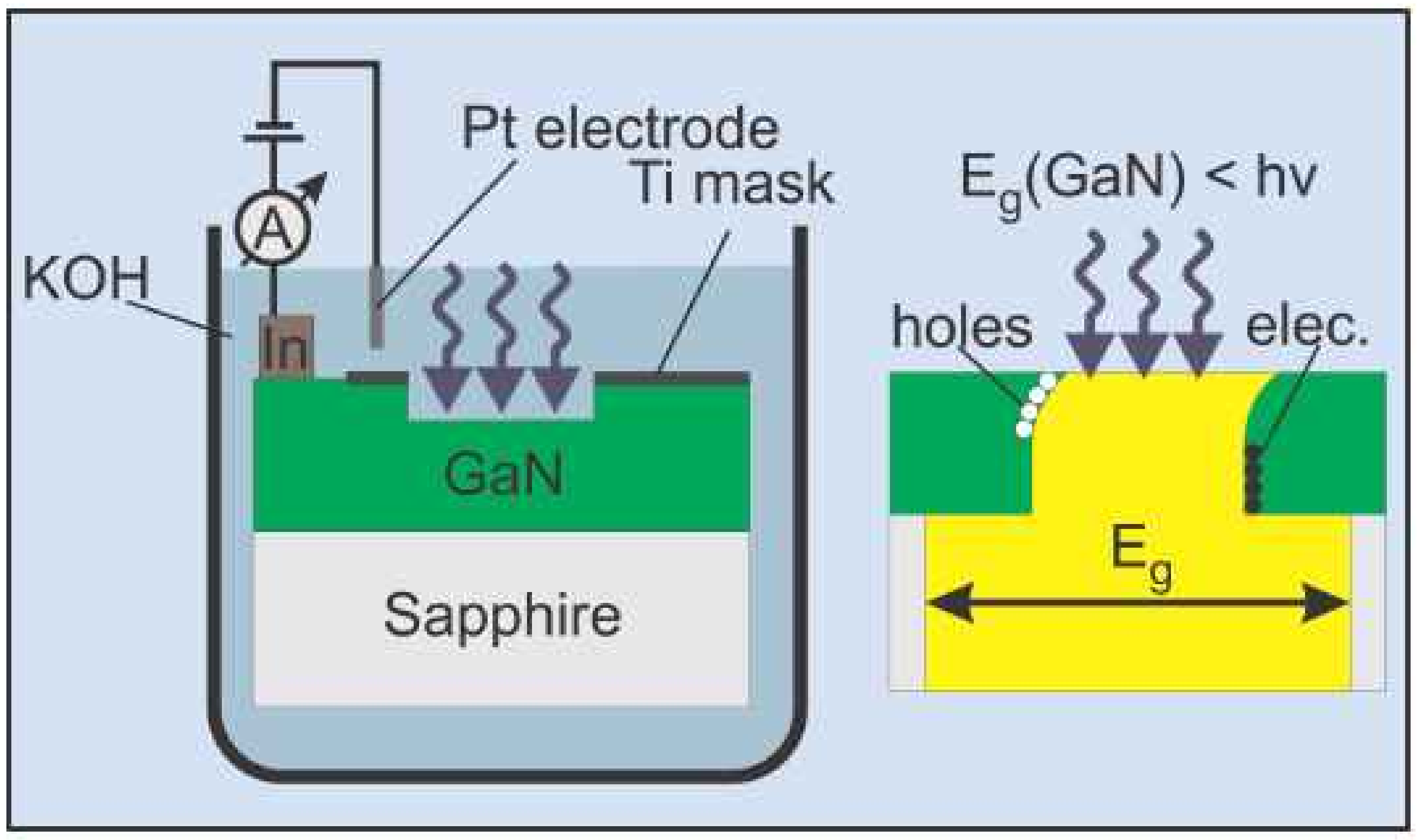

Figure 3. Schematic of photo-etch set-up (left) and band diagram of semiconductor structure under bias producing holes near the surface.

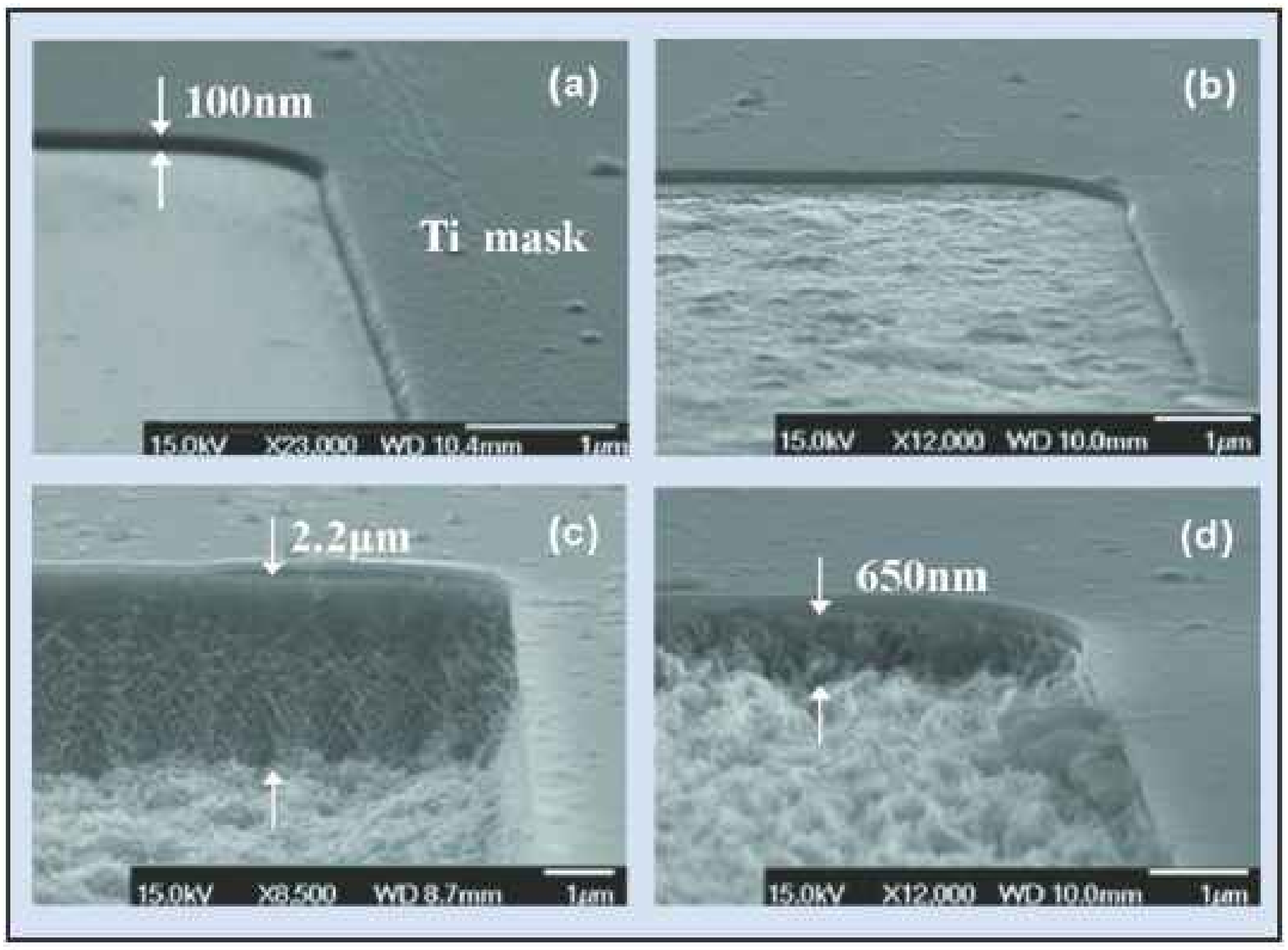

Figure 4. SEM pictures of result of photo-etch process at various stages and under different conditions: Ti patterned GaN sample before etch (a), and when electrochemically etched under illumination at 3.36eV (b), 3.43eV (c), and 3.54eV (d).

In recent work [3], GaN vs AlGaN selective etch has been studied by the researchers from the University of Crete and the Greek Foundation for Research and Technology Institute of Electronic Structure & Laser (FORTH/IESL). The samples were put in an electrochemical cell where a bias can be applied between an anode formed by an indium contact on the GaN film surface and a cathode made of platinum (see Figure 3, left). A 100nm-thick titanium layer patterned with square holes was used as the etch mask.

A Ti:sapphire laser was used to produce 150 femtosecond pulses with a wavelength tuning range of 670–760nm. The nonlinear photonic crystal beta barium borate (BBO) was used to double the frequency of the radiation to the range of GaN's bandgap (~3.4eV).

The researchers measured the photocurrent at various excitation energies and found a resonance around 3.43eV associated with exciton absorption. Excitons are electron–hole bound states that, in PL measurements, produce lines below the main bandgap edge. The exciton enhancement has not been seen before by other groups exploring photochemical etching. The Crete scientists believe that this is due to the excitation sources in these other experiments being more broadband.

The wet etch process actually occurs under a reverse bias that confines holes to the GaN surface where they enable the oxidation of the Ga from the GaN film (Figure 3, right).

Scanning electron microscope (SEM) characterization of the etch results for various frequencies of excitation followed cleaning with a strong KOH solution to remove oxide by-products (Figure 4). The greatest etch depth of 2µm occurred at 3.43eV, while at 3.36eV there was a small amount of roughening of the surface and at 3.54eV the etch process reached down only 650nm.

The researchers investigated the same process with an $\text{Al0}_{.32}\text{Ga}_{0.68}\text{N}$ film with a wider bandgap and found no etching at all at 3.43eV. This selectivity opens up the hope that the process could be useful for processing nitride semiconductors, particularly those requiring optical flatness.

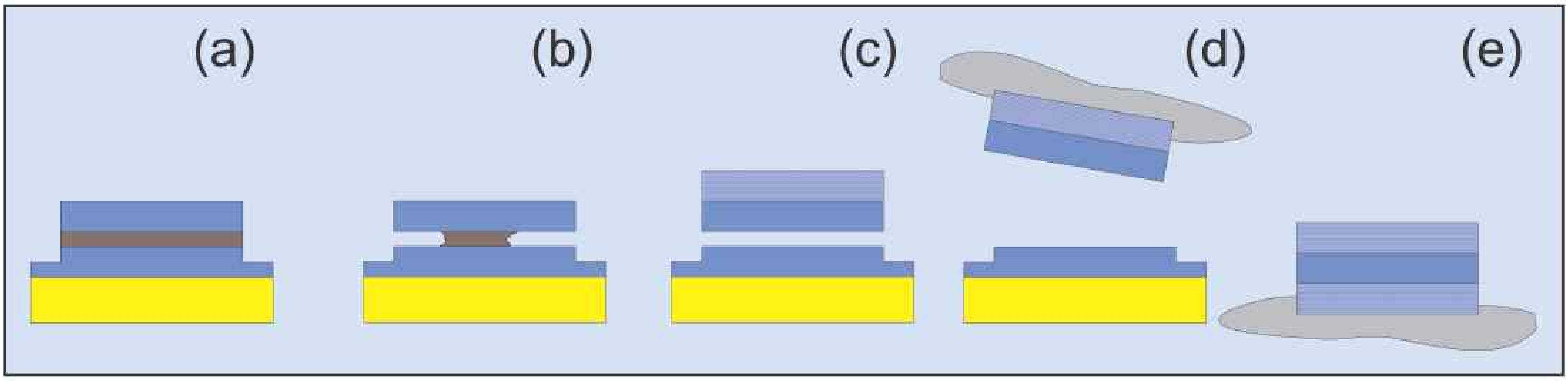

Figure 5. Proposed method for producing distributed Bragg reflectors (DBRs) on a GaN membrane: a mesa is formed using reactive ion etch (a), then an InGaN layer is etched under the top GaN layer using photo-electrochemical method (b), one DBR is then deposited on top of the GaN membrane (c), that is then transferred to carbon tape (d), and flipped to create back-side DBR (e).

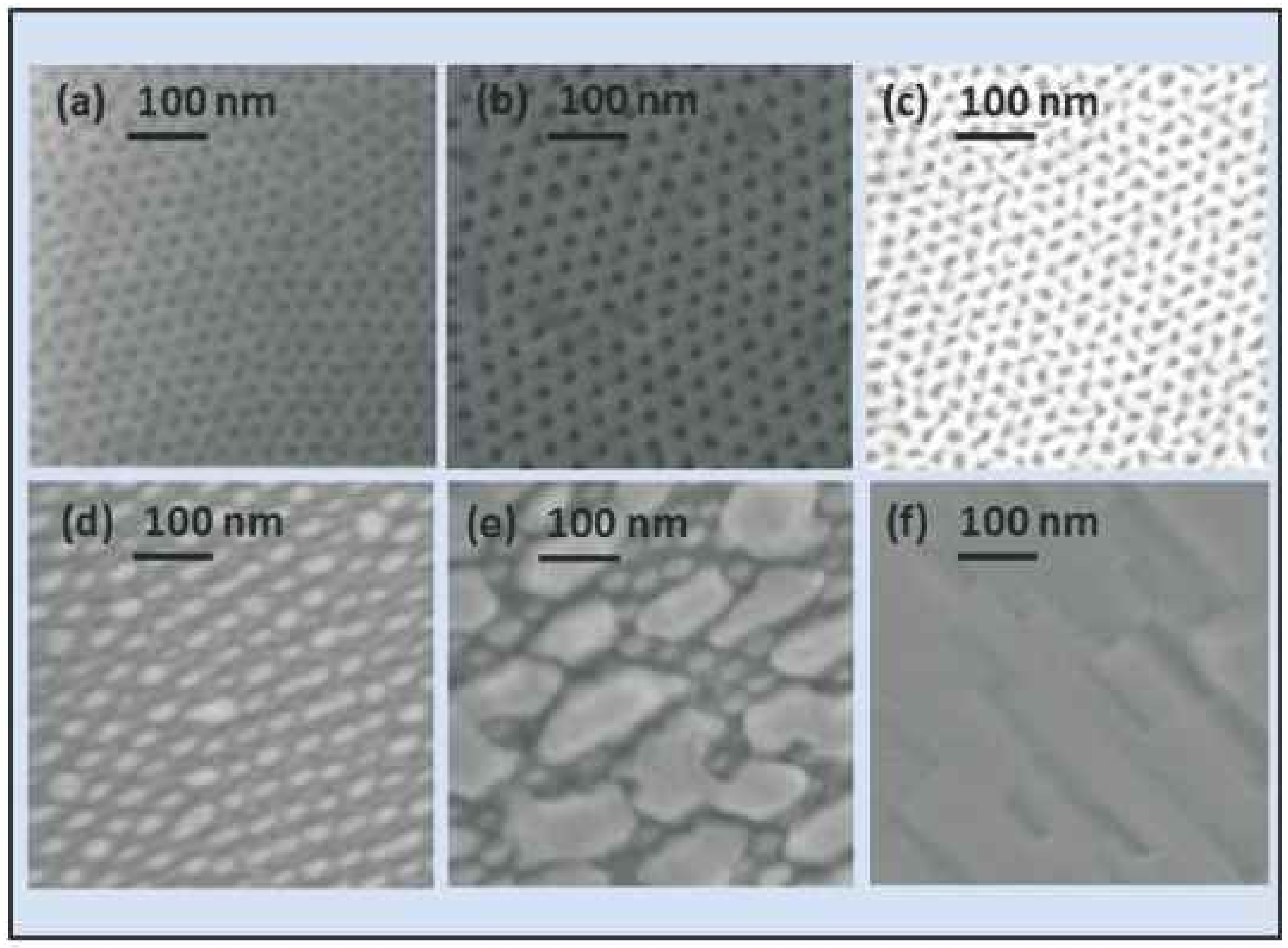

Figure 6. Different stages of using hydroxy-terminated random polystyrene-poly-methyl-meth-acrylate (PS-r-PMMA) copolymer brush material to form hexagonal SiO_2 mask over GaAs substrate (a–c) and then grow 200nm GaSb layer with improved crystal structure (d–f).

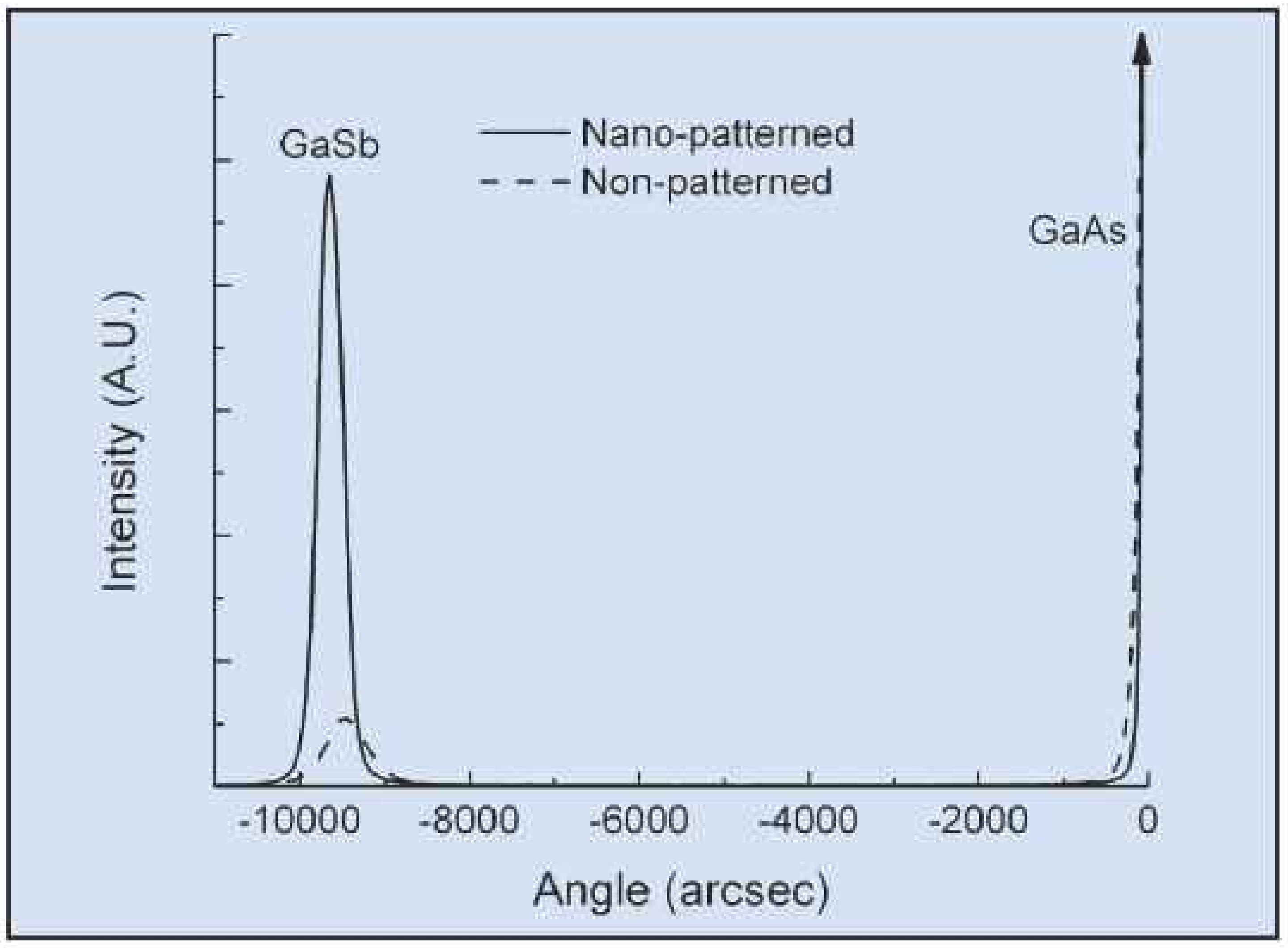

Figure 7. High-resolution x-ray diffraction plot for non-patterned and nano-patterned 200nm GaSb layers grown at 530ºC on GaAs substrate. Plots are normalized to give equal peak height for the GaAs signal. The nano-patterned sample shows a higher, narrower peak, indicating better crystal quality.

A final experiment looked at structures that combined layers of pure GaN with AlGaN. In particular, GaN was deposited on a 100nm layer of $Al_{0.2}Ga_{0.8}N$. The wet etch with ~3.4eV illumination consumed the GaN layer but stopped when it reached the AlGaN. Again, a Ti patterned mask was used.

The Crete researchers are also investigating the possibility of creating high quality factor (Q) nitride microcavities using GaN membranes created from etching away narrower-bandgap InGaN material (Figure 5). It is proposed to form the membranes by etching laterally under mesa structures previously formed by a reactive ion etch. A distributed Bragg reflector would then be deposited on the GaN membrane before transfer to carbon tape. The structure would then be flipped and a second DBR deposited on the other surface of the GaN. A journal article is in preparation describing the formation of the GaN membranes.

The researchers in Crete have been developing the photochemical etch for a while. Last year, they studied the etch technique on separate samples of GaN and AlGaN [4].

Patterns of development

In mainstream semiconductor production on silicon, etch is used to transfer patterns to the growing layers of device structures. This is less common in compound semiconductor growth, where layer structures are built up using MOCVD or MBE. Device structures (LEDs, lasers, transistors, etc.) are then formed only after all the compound semiconductor layers have been deposited. Even where nanostructures are desired, such as quantum dots, dashes or wires, one generally depends on 'self assembly' to create different regions. For example, InAs quantum dots form naturally on a GaAs surface under the correct growth conditions.

One reason for the continuous growth methodology is that it is time consuming (and, in production, costly) to interrupt growth processes for patterning steps. A good reason is therefore needed before a patterning step is considered. Epitaxial lateral overgrowth (ELOG) techniques use windows etched in a layer of material used to block dislocations in nitride semiconductor material from continuing their growth upwards. The dislocations result from the large lattice mismatches (~15%) between sapphire and silicon substrates and the nitride semiconductor material system. GaN material grown from the semiconductor layer exposed by the windows generally exhibits lower dislocation densities.

Researchers at the University of Wisconsin at Madison (UW-Madison) have also used patterning to improve crystal structure for GaSb/GaAs with a poor lattice match (~8%) [5]. These researchers used directed self-assembly of a block copolymer to form a polystyrene mask of ~40nm-pitch hexagonally structured ~20nm holes on silicon dioxide layer on a GaAs wafer (Figure 6). A reactive ion etch using CHF_3/Ar is then used to cut through to the GaAs substrate. The polystyrene was removed using an oxygen plasma. GaSb films grown using tri-ethyl-Ga (TEG) and TE-Sb (TES) on patterned wafers showed improved crystallinity over GaSb films grown using the same process on unpatterned wafers, as shown by high-resolution x-ray diffraction (Figure 7).

UW-Madison has previously used a similar copolymer technique to grow quantum dot structures on InP [6]. Another structuring technique being explored by UW-Madison is to etch through an active layer to create quantum 'boxes' of InGaAs/AlInAs [7].

➤

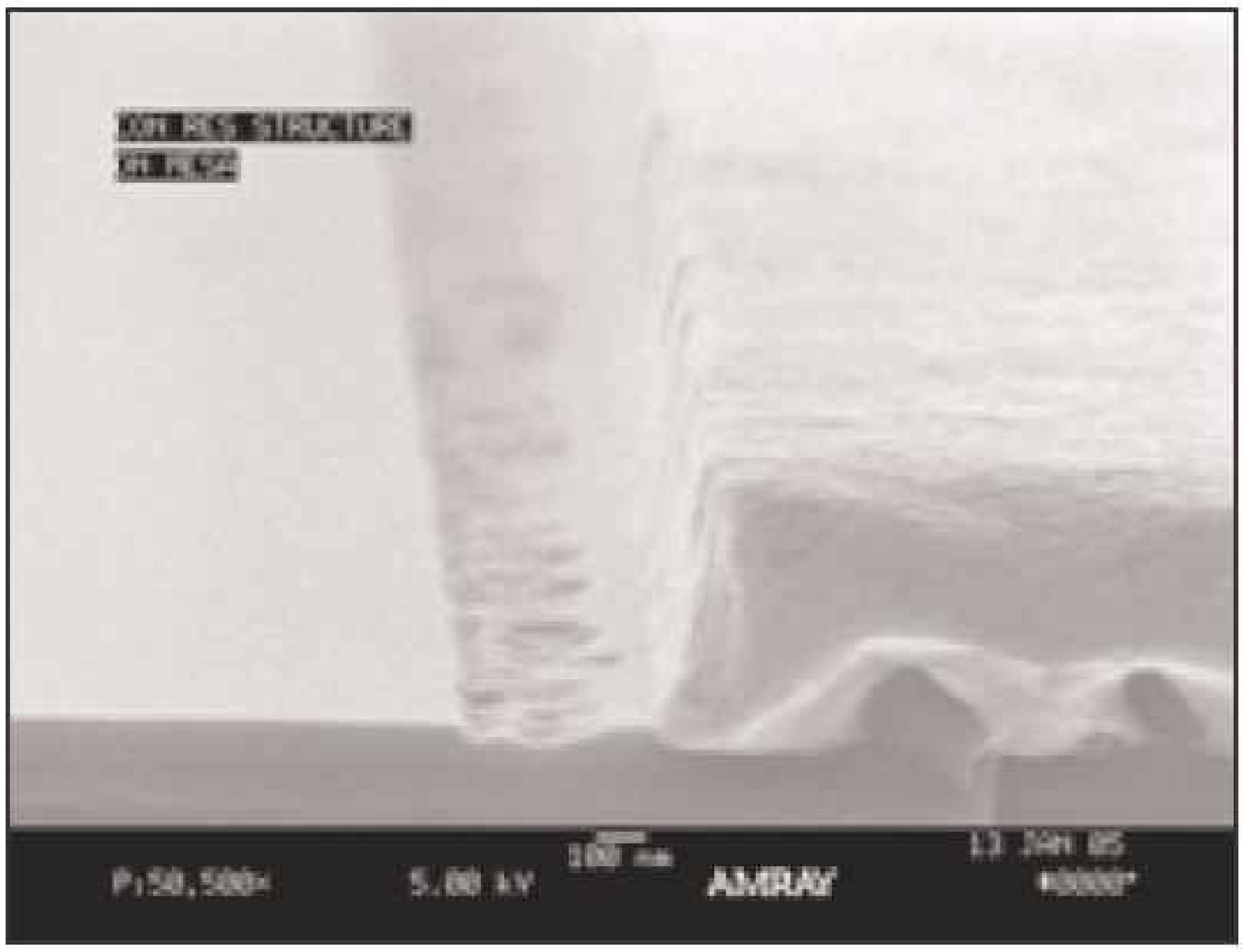

Figure 8. Erosion of n-doped GaAs next to ohmic metal as a result of wet cleaning processes.

Etch not wanted here

Some wet processes cause etching that is not required. Kezia Cheng of Skyworks recently investigated an erosion effect that can occur in producing ohmic contacts (Figure 8) during GaAs transistor production [8]. It is thought that an electrochemical (galvanic) etch effect during wet cleaning processes is the cause. The effect is believed to result from the combination of metals in the contact stack. The erosion tends to cause an increase in contact resistance. In some cases, a two-fold increase in resistance is observed.

Such contacts are typically formed by evaporation of metals onto the wafer, a lift-off process of the excess material, and alloying into the semiconductor material in a thermal process. Cheng carried out tests on three contact recipes: a standard Ni/Au/Ge/Au and a new combination of Ni/Ge/Au that is thermally annealed for alloying in two different ways (Table 1). The wafers used contained AlGaAs/InGaAs/AlGaAs pseudomorphic high-electron-mobility transistor (pHEMT) device structures.

Apart from the metal deposition and thermal annealing, the wafers were subjected to the same processing steps including three treatments with N-methyl-pyrrolidone (NMP) and deionized water rinse, and one ammonium hydroxide (NH_4OH) dip. NMP is an electrolytic solution with potential for electrochemical action, depending on differences in work function between the metal and semiconductor layers. It is after the wet processes that the lightly annealed group of new ohmic metal showed a two-fold increase in contact resistance (post-gate column, Table 2). SEM inspection indicated that trenching had occurred in this group.

A further round of NMP and ammonium hydroxide processing, before process control monitoring (PCM) resistance measurements, created additional contact resistance degradation for the lightly annealed group A and in addition a significant increase for the traditional metal combination of group C. Meanwhile, the more aggressively annealed group B, showed only a small increase in contact resistance through the process.

Cheng performed various focused ion-beam, scanning transmission electron microscope (STEM) and energy-dispersive X-ray (EDX) inspections to analyze the contacts. A high proportion of NiGeAs grains were observed in the group B samples. The other wafers had large gold grains with a larger work function between the noble metal and GaAs, increasing the erosion effect. Cheng believes that the potential difference between adjacent gold and NiGeAs grains also creates an electrochemical action, reducing the rate of reaction on the GaAs surface. The doping level also has an effect, due to a shift of work function, so that on-mesa (highly doped) erosion is less than that off-mesa (lightly doped).

An unwanted side-effect of the reduced contact resistance was a 29% increase in gate leakage in transistors with the new ohmic metal formulation. Skyworks is exploring the causes of the higher leakage currents. However, the on-resistance and third-harmonic over control were improved compared to the traditional metal scheme. ■

Table 1. Contact stack alloying conditions and resistivity measurements at various stages of production process.

Group	Alloying Temp °C	Alloying Time sec	Pre-gate R_{cont} Ω-mm	Post-gate R_{cont} Ω-mm	PCM R_{cont} Ω-mm
A, new ohmic	380	10	0.21	0.47	0.76
B, new ohmic	420	45	0.18	0.23	0.25
C, control	415	200	0.17	0.27	0.4

Table 2. DC and RF test data on contact stacks.

	R_{on} W	Leakage (I_g) mA	Third harmonic dBc
Control	4.6	0.67	67.53
New ohmic	4.3	0.86	70.29

The author Mike Cooke is a freelance technology journalist.

References

1. Zhilai Fang, J. Appl. Phys., vol106, p023517, 2009
2. Fang et al, Nanotechnology, vol20, p045401, 2009
3. Trichas et al, App. Phys. Lett, vol94, p173505, 2009
4. Trichas et al, phys. stat. sol. (a) vol.205, p2509, 2008
5. Smita Jha et al, Appl. Phys. Lett., vol95, p062104, 2009
6. Park et al, p52, Indium Phosphide and Related Materials conference 2009. See also Cooke, Semiconductor Today, p64, September 2009
7. Raithi et al, p.83, IPRM 2009. See also Cooke, Semiconductor Today, p64, September 2009
8. Kezia Cheng, CS Mantech 2009, 'Effects of Ohmic metal on electrochemical etching of GaAs in pHEMT manufacturing'