

Progress at Macquarie University's Low Temperature Nitride Growth Facility

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The Low Temperature Nitride Growth Facility has been formed with the goal of developing novel growth and analysis techniques that may be suitable for the growth of group III nitride materials at temperatures below 650° C. The new growth facility includes three thin film growth reactors, a separate clean room facility, and a plethora of characterisation and device fabrication tools. This paper will outline the present status of the facility but will also highlight some of the recent work by the facilities staff. This includes, the development of an AFM based piezoelectric measurement system; the development of sub-growth temperature re-crystallisation techniques for the improvement of low temperature grown gallium nitride [1]; progress in the development of indium nitride – a material pioneered in Australia. What is the band-gap of indium nitride? Is it 0.7 eV or is it 1.89 eV [2]? And finally the development of ultra-high resistivity aluminium nitride layers grown at room temperature is reviewed [3].

1. Introduction

Aluminium nitride and gallium nitride are usually grown at temperatures above 900° C [4]. Gallium nitride has become a particularly important material for lighting applications, but is typically grown on expensive sapphire substrates. For high power lighting complex device structures are also required for the growth of high quality nitride layers on sapphire. The Luxeon product range of the U.S. company LumiLed represents state of the art for white light development. LumiLed use yellow phosphors with a blue LED to produce white light. They have achieved 187 lumens per LED at a maximum efficiency of 44.3 lumens/watt [5]. This compares to about 18 lumens/watt for incandescent lights and 85 lumens/watt for fluorescent lights. Although gallium nitride is well established in many specialized lighting areas, to be competitive for room lighting, production costs must be reduced by 50 times their present level. Similarly the production of GaN based lasers is hampered by the difficulty, or rather complexity, of the growth procedures that are required to reduce dislocation defects to tolerable limits. Though these lasers are now manufactured reproducibly, and new DVD formats are being established in anticipation of using GaN based lasers, their high cost (AUS\$1000- \$2000) has so far limited their application. A similar story exists for the production of high frequency GaN transistor devices, where the technology is still emergent and considerable effort is required to overcome the problem of lattice defects that ultimately result from the lattice mismatch with SiC and sapphire substrates.

Therefore, it can be seen that the main cost detractors for the use of GaN are equipment costs for high temperature growth; the cost of sapphire and SiC substrate materials, and the high cost of producing complex growth structures on these substrates. Low temperature growth on other materials more closely lattice-matched to GaN, such as ZnO, may provide a solution to these problems.

The Macquarie University Low Temperature Nitride Growth Facility has been established to address the issues of both the temperature and cost requirements of present nitride technology. The center piece of the facility is a cutting edge nitride growth system, which is a wholly

unique combination of thermally controlled metalorganic chemical vapour deposition (MOCVD), remote plasma enhanced chemical vapour deposition (RPECVD) and laser induced chemical vapour deposition (LICVD). This new type of growth system has been given the acronym RPE-LICVD, which recognizes the combination of growth methodology that we have found most successful for low temperature GaN growth [1,6]. Pulse laser deposition using an ArF UV laser, operating at 193 nm, is also possible in this system [7].

There are few other film growth systems in the world that achieve the degree of flexibility, and accessibility of growth parameters, that this combination of low temperature growth methods achieves. The new system is the second generation of this implementation of RPE-LICVD, and is an ultrahigh vacuum (UHV) turbopumped system that incorporates a load lock with sample transfer system; a rotating heater stage capable of accepting 2 inch substrates (at present the standard substrate size for GaN growth); an independently pumped residual gas analyzer for gas analysis and a UHV gas delivery system for the growth of InN, GaN, AlN and their alloys. Dopants for the system will be fully on line this year and include sources for carbon, magnesium, silicon and oxygen doping.

In the following sections we provide an overview of some of the recent achievements of members of the Low Temperature Nitride Growth Facility. We briefly examine one of the characterization tools being developed for nitride analysis – piezoresponse force microscopy. A technique used to image the piezoelectric response of thin films on the scale of an atomic force microscope. We then report on some early results for what may become a major breakthrough in GaN film growth – the low temperature re-crystallisation of RPE-LICVD grown films. The facility staff, particularly T. L. Tansley, have a long history in InN research, and that work remains active. International interest in InN has escalated substantially in the last 2 years, and an important debate on the properties of InN has recently erupted. In particular the band-gap of this emergent material is being disputed. Although recent reports suggest a 0.75 eV band-gap we show that the 0.75 eV feature may well be a sub-band-gap feature, and that the absorption spectra for material recently grown overseas, may originate from a defect related energy level for material with a 1.9 eV band-gap. Finally we report on AlN grown at room temperature with properties superior to PECVD grown silicon nitride, and suggest that this particular AlN may have excellent potential in industrial applications as a dielectric or passivating layer for nitride based device structures.

2. Piezoresponse Force Microscopy

In recent times, scanning force microscopy has been used to measure piezoelectric activity with high spatial resolution [8,9]. While usually applied to materials with large piezoelectric coefficients, such as lead zirconate titanate, the technique has recently been applied to GaN [10]. Conventional piezoelectric measurements measure the average response over some area of material. The AFM technique provides an opportunity to measure polarisation on a spatial scale consistent with the size of individual crystallites.

Figure 1 shows the piezoelectric response along a single scan line, in both LiNbO₃ and GaN, with 5.0 V applied to the sample and the same gain settings. The relative variation in piezoelectric response across the single crystal LiNbO₃ wafer is much smaller than for the polycrystalline GaN. Also the magnitude of the LiNbO₃ response is much larger.

The magnitudes of the piezoelectric responses, as shown in the line plots of figure 1, give an indication of the relative size of the piezoelectric coefficients in LiNbO₃ and GaN. The large variation in the GaN plot results from the polycrystalline sample. This possibly explains why various polycrystalline GaN samples show a large variation in their macroscopic piezoelectric coefficients and why polycrystalline samples show a lower macroscopic coefficient than single crystal material [11].

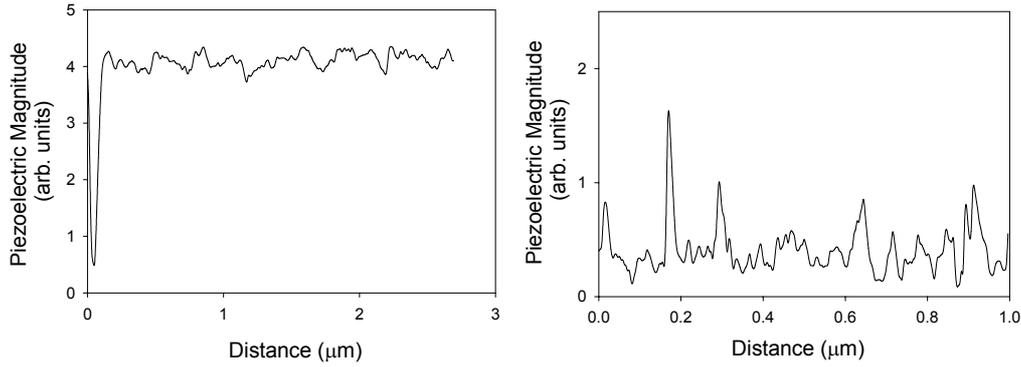


Fig. 1. Piezoelectric response along a line across the sample for (a) single crystal LiNbO₃ wafer and (b) polycrystalline GaN

3. Low Temperature GaN Recrystallisation

Because of its small lattice mismatch to GaN (~1.8%), ZnO is an attractive potential substrate material for the growth of GaN [1]. However, growth in the ammonia environment typically used for GaN must occur at low temperatures - below approximately 650 °C - otherwise the ZnO would dissociate. We have applied the RPE-LICVD technique to GaN growth on ZnO with some success, however at these low growth temperatures polycrystalline material is usually grown (or at least when using the high vacuum environment of the earlier generation RPE-LICVD unit [6] -further growth investigation is required with the new system). Very recently, we have observed that GaN grown by this technique, at temperatures as low as 570° C, may be recrystallised below the film growth temperature. The methodology is the subject of patents. Figure 2 shows the change in the surface profile of recrystallised samples, compared to the original morphology (figure 2 a). The images were collected by

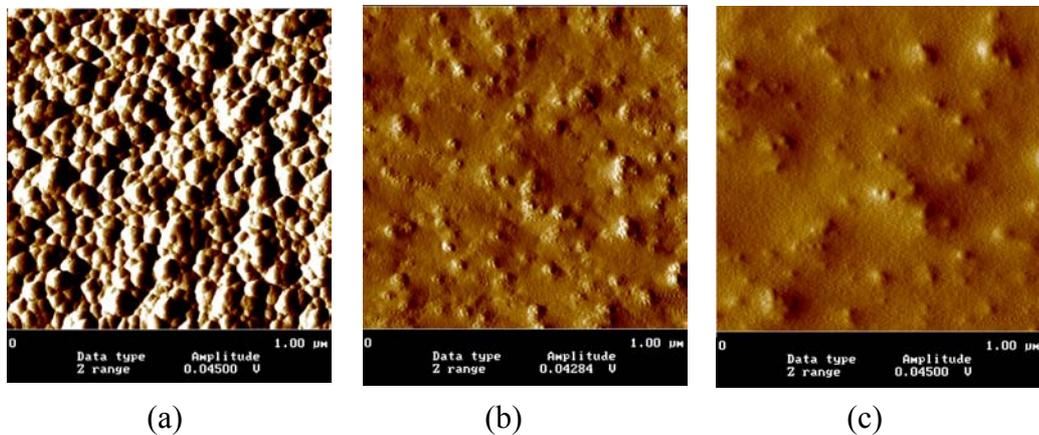


Fig. 2. AFM error mode images of GaN sample surfaces. Image (a) is an unprocessed sample –this image is typical of the “as grown” samples. Images (b) and (c) show samples at various degrees of crystallisation.

atomic force microscopy. Other evidence of the re-crystallisation process is provided elsewhere [1], though it is noted that improvement in X-ray diffraction peak width (a reduction in the peak width indicating improved crystallinity) and electrical conductivity have also been measured.

The significance of this work is that a low defect density GaN layer might be achieved for subsequent device processing with very little effort and cost compared to present methodologies.

1. The Band-gap of Indium Nitride

Indium nitride is potentially a very high mobility material, but many of its basic properties are still being assessed. A group of low carrier concentration polycrystalline thin films were grown by members of the Low Temperature Nitride Growth Facility by RF sputtering in the early 1980s, with one having the highest reported room temperature n-type mobility ever produced for indium nitride: $2700 \text{ cm}^2/\text{V}\cdot\text{s}$ for a carrier concentration of $5 \times 10^{16} \text{ cm}^{-3}$ [12]. That material had a measured band-gap of 1.89 eV [13] and has formed the basis of the accepted band-gap since that time.

More recently MBE InN has been grown by a number of groups with much lower apparent band-gaps, reported as being as low as 0.7 eV [14-16]. Photoluminescence data for InN is very rare and the 0.7 eV band-gap groups have demonstrated photoluminescence at approximately that energy. However, other independently grown MBE material has shown photoluminescence at 1.9 and 2.1 eV [17], so that the debate cannot be characterized as MBE versus RF sputtering.

The most compelling data for an ~ 0.75 eV band-gap has been reported by Wu et al. [14] where photoluminescence, absorption and photoreflectance data are all alleged to indicate a 0.7-0.8 eV band-gap. There are many sub-band-gap mechanisms for photoluminescence, and the photoreflectance spectrum of Wu et al. [14] is too weak to provide a plausible proof on its own. The absorption data at first glance appears most compelling. In Figure 3 we have replotted the absorption coefficient (α) data of Wu as absorption squared. This is the common type of plot used to determine the band-gap energy of direct band-gap semiconductors, and it is immediately apparent, from the usual extrapolation of the linear region to the x-axis, that the absorption data indicates a 0.98 eV band-gap, not a 0.75 eV band-gap as suggested by Wu. The observed photoluminescence would therefore also appear to be a sub-band-gap feature below the 0.98 eV absorption feature. In addition to this we have also plotted in Figure

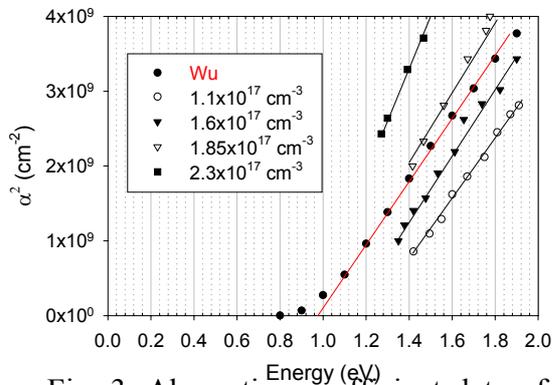


Fig. 3. Absorption coefficient data of Wu [14] replotted as absorption coefficient squared with data presented previously by Tansley and Foley for a trap related subband-gap absorption level.

3 absorption coefficient squared data from Tansley and Foley [18]. In the case of Tansley and Foley their absorption data was observed to be a sub-band-gap absorption that those authors attributed to $|p\rangle$ like orbital defect states. Whether the transition, most recently observed at 0.98 eV represents a sub-band-gap or direct band-gap feature seems to be the question that now requires answering.

We have recently also shown that the MBE InN supplied by two of the groups supporting a ~ 0.75 eV band-gap show strong inter-diffusion of Al and In at the InN layer interface. The inter-diffusion was observed for samples where the InN was deposited on either sapphire or an AlN buffer layer, though the inter-diffusion appeared to be worse for samples grown on an AlN

buffer layer. This interdiffusion was shown to be so severe that the absorption data for the samples that had been measured were affected. We have reported this data in further detail elsewhere [2].

2. Ultra-high Resistivity Aluminium Nitride

Aluminium nitride layers have been grown by our group using novel RPECVD based techniques. Figure 4 shows a current density versus applied electric field for a 93 nm thick AlN metal-insulator-metal (MIM) device, where the AlN layer was grown at room temperature. Film resistivities of $3.3 \times 10^{16} \Omega \cdot \text{cm}$ are three orders of magnitude higher than is typically reported for AlN, and an order of magnitude higher than is typical for PECVD grown silicon nitride. Silicon nitride is widely used in the silicon industry as a thick dielectric layer. The film breakdown field was as high as 640 MV/m, which is comparable with PECVD grown silicon nitride. These exceptional results were obtained using ultraviolet photolytic desorption techniques reported elsewhere [3,19]. However, we can report here that films previously tested to irreversible breakdown had self-repaired when examined some 18 months after the initial work. The films were able to be taken to fields in excess of 200 MV/m without further breakdown. Testing to the breakdown point was not attempted after the device recovery.

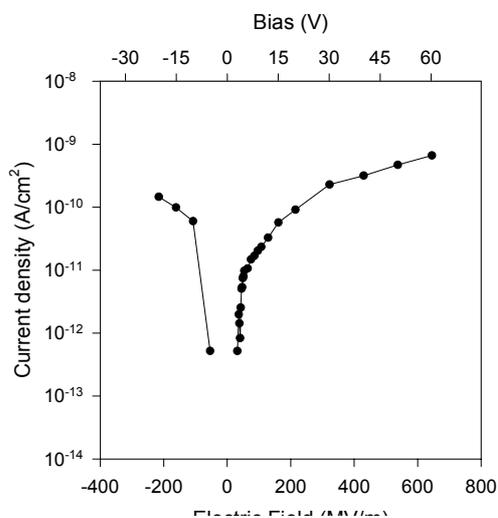


Fig. 4 Current density versus electric field for AlN MIM structure. The AlN was 93 nm thick and had a maximum bias of 60 V applied to it before breakdown occurred.

The excellent results achieved in improving the insulating properties of AlN have encouraged us to promote this work further with the aim of improving the growth rate for use in industrial semiconductor processing, particularly – though not exclusively - in the growing area of nitride device technology.

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