

Plasma-assisted molecular beam epitaxy process combined with a liquid phase electroepitaxy, a novel method for the growth of GaN layers



S.V. Novikov*, R.E.L. Powell, A.J. Kent, C.T. Foxon

School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, UK

ARTICLE INFO

Available online 15 January 2013

Keywords:

A3. Liquid phase epitaxy
A3. Molecular beam epitaxy
B1. Nitrides
B2. Semiconducting III–V materials

ABSTRACT

We have studied a novel approach for the growth of GaN layers, namely plasma-assisted electroepitaxy (PAEE). We have designed and built a new growth chamber which allowed us to combine a plasma-assisted molecular beam epitaxy process with a liquid phase electroepitaxy. We have demonstrated that it is possible to grow continuous GaN layers by PAEE from a liquid Ga melt at growth temperatures as low as $\sim 650^\circ\text{C}$, with low nitrogen overpressures of $\sim 3 \times 10^{-5}$ Torr.

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1. Introduction

In conventional growth by plasma-assisted molecular beam epitaxy (PA-MBE) of group III nitrides, it is now well established that the highest quality GaN layers can be grown under Ga-rich conditions [1]. Whilst the solubility of molecular nitrogen in Ga under normal growth conditions is very low, because the process is dissociative with a high energy barrier, the solubility of activated nitrogen species in Ga is expected to be relatively high [2,3]. If this model is correct, the growth process of GaN in PA-MBE is not like conventional molecular beam epitaxy, but more like liquid phase epitaxy (LPE), driven by a constant supply of active nitrogen [2,3]. Data on the growth rates of GaN layers by PA-MBE show that activated nitrogen from a plasma source can be used to produce relatively high concentrations of N in a Ga-based melt.

Solution growth methods are normally used in the commercial production of standard III–V crystals with low dislocation density. However, the solubility of N in liquid Ga is very low and therefore it is difficult to obtain reasonable growth rates of GaN from liquid Ga. Several groups worldwide have tried to use N-plasma sources to increase nitrogen solubility. Unfortunately, this high concentration of N exists only close to the surface of the metallic Ga and normally results in spontaneous crystallisation of polycrystalline GaN on the surface of metallic gallium [4]. In order to achieve an efficient epitaxial growth process with use of the N-plasma sources one needs to develop a technique to transport the N species through the gallium melt to the growth surface and at the same time to minimise spontaneous nucleation.

Liquid phase electroepitaxy (LPEE) is a crystal growth method for III–V layers in which the layer growth is initiated and sustained by passing a direct (DC) electric current through the liquid metal solution–substrate interface while the growth temperature of the overall system is maintained constant [5].

We have already demonstrated that the LPEE configuration can be used in Ga–N solutions [6]. We have established that an electric current passing through the GaN/Ga–melt interface in the appropriate direction allows us to increase the etching rate for GaN. We have used electromigration from the interface and Peltier heating of the interface in order to form a concentration gradient for N species away from the etching surface.

Recently we have studied a novel approach for the growth of GaN layers, namely plasma-assisted electroepitaxy (PAEE) [7,8]. We designed and built a new vacuum growth chamber which allowed us to combine the plasma-assisted molecular beam epitaxy process with liquid phase electroepitaxy. In the PAEE method, we have combined the advantages of the plasma process in producing high concentrations of N species in the Ga melt with the advantages of electroepitaxy in transferring the N species from the Ga surface to the growth interface, without spontaneous crystallisation on the surface or within the solution. We demonstrated that it is possible to achieve GaN nucleation on sapphire substrates by PAEE at growth temperatures as low as $\sim 450^\circ\text{C}$ [7,8]. We initially performed the growth on (0001) sapphire substrates, because this demonstrates unambiguously the possibility of the PAEE process working. Sapphire is not soluble in the Ga melt. However, a potential problem with sapphire substrates is the difficulty of wetting of sapphire with liquid gallium. We observed clear evidence for the formation of GaN nucleation islands on the surface of sapphire substrates after PAEE growth times of about a few hours. In an optical microscope we were able to see a random local nucleation on large areas of the surface. We confirmed the GaN growth using XRD and PL studies [7,8].

* Corresponding author. Tel.: +44 115 9515138; fax: +44 115 9515180.
E-mail address: Sergei.Novikov@Nottingham.ac.uk (S.V. Novikov).

However, we also observed areas without nucleation on the surface due to only partial wetting of sapphire by the Ga melt. The aim of the current study is to look at PAEE growth of GaN and InN layers on GaN templates.

2. Experimental details

We have designed and built a new growth chamber which allows us to combine the PA-MBE process with LPEE [7,8]. The PAEE growth chamber is made of stainless steel and has a water jacket to remove the heat. We have used an Oxford Applied Research HD60 RF plasma source to generate active nitrogen in our plasma-assisted electroepitaxial (PAEE) system. The plasma source has a beam diameter of ~ 50 mm, which allows us to achieve a uniform N-flux over the entire Ga melt surface. In the chamber the RF plasma source is mounted directly above the boat containing liquid Ga. The boat with liquid Ga is positioned on the top of the heater, which allows us to change the temperature of the PAEE epitaxial process. The boat is made of graphite and pyrolytic boron nitride (PBN). The diameter of the Ga melt is 10 mm. The height of the Ga melt used in the current study is about 3.5 mm, which is slightly more than the thickness of the 2 mm PBN slide and is the minimum height that allows us to establish a stable electrical contact to the top graphite slide of the boat. The substrates are about 5×13 mm². Therefore the area of epitaxy is limited by the size of the Ga melt and is about 5×10 mm². In this particular study, the electric current goes through the liquid Ga, but not through the insulating GaN/sapphire substrate. The design of the boat allows us to outgas the Ga melt before it comes into contact with the epitaxial substrate.

In the current study we have used GaN templates grown on (0001) sapphire by metal–organic vapour phase epitaxy (MOVPE) as substrates in order to improve the wetting of substrates by liquid Ga. The MOVPE GaN layers have a thickness of ~ 2 μ m and were doped with Si to achieve n-type conductivity $\sim 10^{18}$ cm^{−3}.

The growth temperatures for PAEE growth were about 650 °C. Before performing PAEE growth, we have outgassed the gallium in vacuum ($\sim 10^{-7}$ Torr) for 30 min at temperatures of ~ 650 °C. After that we move the Ga melt into contact with substrate, start the DC current, introduce high purity nitrogen gas into the chamber and strike the plasma to start the PAEE process. In all experiments present in this paper we have used a chamber pressure of $\sim 3 \times 10^{-5}$ Torr and 500 W power for the RF plasma source. We have used DC current of 50 A with negative polarity to the Ga melt. At the end of the PAEE process the Ga melt was removed from the surface of the substrate at the growth temperature and the system cooled to room temperature. Any remaining traces of Ga were removed from the substrate surface by the standard chemical HCl-based etching technique.

To investigate the optical properties of GaN layers we have studied photoluminescence (PL) using a frequency-quadrupled Ti–Sapphire laser. The excitation wavelength was 210 nm and the excitation power density approximately 10 W cm^{−2}. PL was measured using a UV fibre-coupled CCD spectrometer.

3. Results and discussion

Fig. 1a shows a scanning electron microscopy (SEM) image of the surface of the sample after PAEE growth of GaN on a GaN MOVPE template for ~ 15 h with a current of 50 A. On the GaN template we obtained uniform GaN nucleation across the surface. The density of the GaN nucleation islands on the GaN templates is higher than on sapphire [7,8] and the dimensions of the GaN

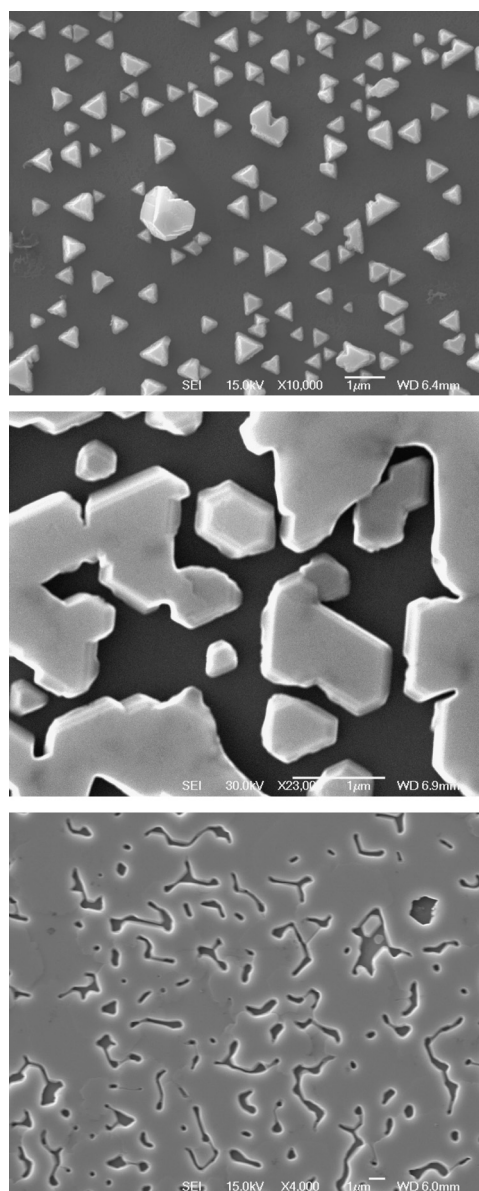


Fig. 1. SEM images of the surface after the growth of GaN on a GaN template by PAEE for ~ 15 h (a), 24 h (b) and ~ 60 h (c).

islands are ~ 0.5 μ m. The shape of the GaN islands is mainly triangular. The other major difference from the growth on a clean sapphire substrate [7,8] is that these triangles are well aligned to the crystallographic orientation of the underlying GaN template as can be seen from Fig. 1a. For initial samples grown on sapphire substrates [7,8], we were able to study XRD and PL. However, on the samples grown on GaN templates, because the composition of the GaN islands and underlying GaN template is the same, this is difficult.

By increasing the growth time of the PAEE process, we were able to achieve coalescence of the GaN islands. Fig. 1b and c shows SEM images of the surface of GaN layer after PAEE growth for 24 and 60 h respectively. In some areas of the surface (Fig. 1c) we observed close to complete coalescence of the islands with just a few remaining holes. Other areas have demonstrated complete coalescence and the growth of a continuous GaN layer. We have observed step flow growth of the PAEE GaN layer after coalescence. These results confirm that it is possible to achieve continuous GaN layers from the Ga melt by PAEE even at low

growth temperatures $\sim 650^\circ\text{C}$ and low nitrogen overpressures $\sim 3 \times 10^{-5}$ Torr.

Fig. 2 shows the low-temperature photoluminescence (PL) from the surface of the MOVPE GaN template and from the two PAEE samples grown for 15 and 60 h. The GaN template PL consists of a broad feature centred at about 3.48 eV, the shape of which suggests that it is composed of two or more spectral lines that are not clearly resolved by the spectrometer. These PL features are consistent with previous measurements of undoped wurtzite MOVPE GaN layers [9]: the feature centred on 3.48 eV probably consists of free exciton and shallow donor and acceptor bound exciton lines; the 3.2 eV line has been attributed to an exciton bound to a point defect; the 3.28 eV line could be a free electron to acceptor transition; and the 3.39 eV feature is probably LO phonon related. In the case of the two PAEE samples, the same lines appear to be present, but in different proportions and a strong additional line appears at 3.46 eV. Clearly the type and density of native defects in the low temperature PAEE samples grown from liquid gallium will be different from those of the GaN templates, giving rise to some changes in spectra. The extra line at 3.46 eV appears to be the “two electron satellite” associated with silicon or oxygen defects.

It is well established that in group III liquid metals, used for LEEF of III–V layers, most of elements migrate towards the anode [5]. There are two possible causes of electromigration. The first one is the ionic contribution, which is normally weak for the standard GaAs-based III–Vs [5]. The second is the momentum exchange between electrons moving towards anode and the solute species. This is the main effect in electromigration for the standard GaAs-based III–Vs [5]. Therefore, we have used negative polarity to the Ga melt in the above PAEE experiments. Nevertheless, we have tried reversing the polarity of the DC current and we observed some nucleation density of GaN crystals. However, such crystals did not coalesce for similar times of the process, but instead led to a three dimensional growth mode. The reason for the nucleation under reverse DC polarity is probably convection in the Ga melt. A DC current of either polarity will increase convection in the Ga metal solution and therefore will increase the transport of N-containing species in the solution. The generation of convection will be even stronger in our PAEE configuration due to the non-uniform lateral distribution of the current in the Ga melt.

In our previous PAEE studies at low growth temperatures $\sim 450^\circ\text{C}$, we did not observe any significant changes in the Ga

melt during and after the PAEE process [7]. However, after PAEE at $\sim 650^\circ\text{C}$ we found a change in the density and viscosity of the Ga melt. We suspect that the change in viscosity is the result of the GaN microcrystals in the melt, but so far we did not prove this experimentally.

The growth of bulk InN crystals is still an unsolved problem. Therefore, we have tried to use our PAEE approach as a new method for the growth of InN layers and crystals. The PAEE growths were performed on GaN templates; we just replaced pure Ga solutions with pure In solutions. The rest of the PAEE procedure was the same. InN is unstable at temperatures above $\sim 550^\circ\text{C}$. To avoid potential damage to the InN, we did not remove the In metal solution from the surface of the substrate immediately after termination of the growth, but after cooling the boat below $\sim 500^\circ\text{C}$. Fig. 3 shows scanning electron microscopy (SEM) images with different magnifications of the surface of the sample after PAEE of InN on a GaN MOVPE template for 3 h with a current of 50 A. We can clearly observe the formation of the bulk microcrystals with hexagonal symmetry, as can be seen from the shape of the crystals. In the case of InN we did not observe a uniform formation of the crystals over the whole surface area as observed in the case of GaN growth (see Fig. 1a). Instead we have the formation of small bulk microcrystals only in local areas on

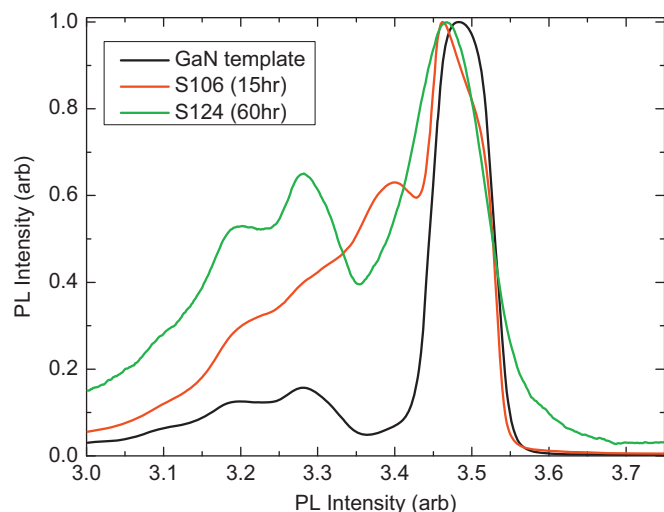


Fig. 2. Low temperature (~ 4 K) PL data for GaN MOVPE template and GaN layers grown by PAEE for 15 h and 60 h.

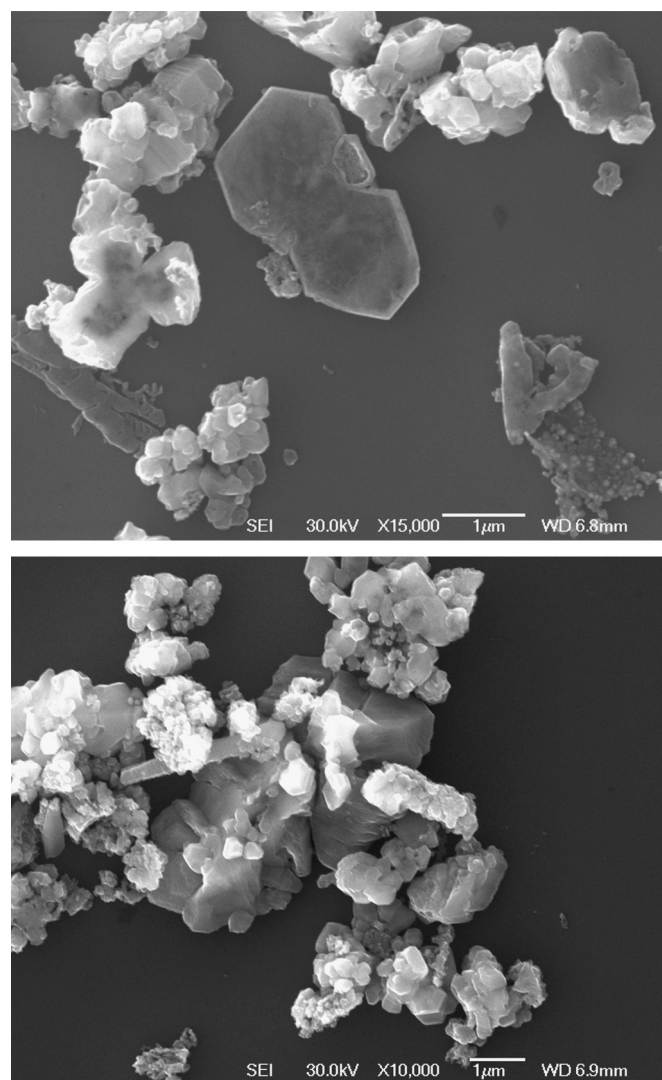


Fig. 3. SEM images of the surface after the growth of InN on a GaN template by PAEE for 3 h.

the substrate and these crystals are grouped together. We are currently investigating the properties of these microcrystals and the results will be published separately.

Growth rates of GaN achieved by our PAEE method are currently very low and the uniformity is poor. But the goal of this initial study was to test the feasibility of this novel PAEE growth approach for GaN epitaxy. The next stage of our research will be to study PAEE in a modified configuration where the DC current passes through the melt–substrate interface to improve the uniformity of the GaN layer. In order to increase the growth rate, we will also increase the growth temperature, which should increase the solubility of the N in the Ga melt. The system, we have developed, will also allow us to use different compositions of the Ga-based melt, for example a Ga–Na melt, which can increase further the solubility of N in the melt.

4. Summary and conclusions

In the current study we have demonstrated the feasibility of a novel approach for the epitaxial growth of GaN layers, namely plasma-assisted electroepitaxy (PAEE). We have designed and built a new growth chamber which allows us to combine the PA-MBE process with LPEE. We have demonstrated that it is possible to achieve the growth of GaN nucleation islands on GaN templates by PAEE even at low growth temperatures and low nitrogen overpressures. We have demonstrated the coalescence of the GaN islands into a continuous GaN layer with increasing PAEE growth time. The exact mechanisms, which led to the growth of

GaN in PAEE, still need to be investigated. However, the first growth results form the basis for the future development of a novel plasma-assisted electroepitaxy (PAEE) process for the growth of GaN layers.

Acknowledgements

This work was undertaken with support from the EPSRC. We want to thank J. Chauhan and C.J. Mellor for SEM studies, and M.J. Kappers and C.J. Humphreys for the MOVPE GaN templates.

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