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# Reduced Workfunction Intermetallic Seed Layers Allow Growth of Porous n-GaN and Low Resistivity, Ohmic Electron Transport

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KEYWORDS: porous GaN, ohmic electron transport.

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3 ABSTRACT. Porous GaN crystals have been successfully grown and electrically contacted  
4 simultaneously on Pt- and Au- coated silicon substrates as porous crystals and as porous layers.  
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8 By the direct reaction of metallic Ga and NH<sub>3</sub> gas through chemical vapor deposition,  
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10 intermetallic metal-Ga alloys form at the GaN-metal interface allowing vapor-solid-solid seeding  
11 and subsequent growth of porous GaN. Current-voltage and capacitance-voltage measurements  
12  
13 confirm that the intermetallic seed layers prevent interface oxidation, and give a high quality  
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15 reduced workfunction contact that allows exceptionally low contact resistivities. Additionally,  
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17 the simultaneous formation of a lower workfunction intermetallic permits ohmic electron  
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19 transport to n-type GaN grown using high workfunction metals that best catalyze the formation  
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21 of porous GaN layers and may be employed to seed and ohmically contact a range of III-N  
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27 compounds and alloys for broadband absorption and emission.  
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## 1. INTRODUCTION

GaN and its related alloys such as InN and AlN that span the UV-VIS-NIR spectrum have received much attention in the realization of new devices for electronics, microwave and optoelectronics/photronics applications. With large bandgap energies, high breakdown fields, large carrier velocities and a tolerance to high junction temperatures, the nitrides have a myriad of possibilities, including LED's,<sup>1</sup> lasers for reading or storing data on high density optical media, solar blind detectors, biological monitoring, gas sensing,<sup>2</sup> and high temperature/high power electronics.<sup>3</sup>

The discovery of light-emitting nanoporous Si<sup>4</sup> propelled investigations of porosity formation in III-V and Group IV semiconductors.<sup>5-7</sup> Their unique properties compared to their bulk counterparts<sup>8</sup> have advanced their use in sensors, interfacial structures, biomedical and catalysis applications.<sup>9-11</sup> Generally, pore formation in semiconductors can be obtained by anodizing them in a suitable electrolyte, under proper conditions,<sup>12</sup> however the ability to form relatively uniform, crystalline porous GaN layers over large areas through complex etching without photolithographic masking or processing is challenging. For GaN, both wet and dry etching techniques have been unsuccessful in forming unique structures of the material and these methods can infer unwanted interface states and surface contamination that can affect transport properties by rendering the GaN surface more resistive. The double issue of dry etching techniques increasing GaN resistivity and wet etching techniques not as crystallographically controllable for GaN as it is for other III-V semiconductors, for example, can be alleviated by other growth methods involving seeding processes, some of which, as will be shown here, allow crystallographically delineated porous layers with improved contact resistivities.

Until now, nanoporous GaN thin films have received particular interest as buffer layers or templates for heteroepitaxial growth of lattice-mismatched materials with low defect density.<sup>13-15</sup>

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3 The porous material decreases the number of defects in the epitaxial layer, even when the lattice  
4 mismatch between the substrate and the GaN epitaxial layer is large, and it furthermore allows  
5 the growth of stress-realized epitaxies.<sup>1</sup> Extensions to wider and narrow gap InN and AlN,  
6 respectively, would allow the possibility of operation from the UV to IR wavelengths, and these  
7 materials are beginning to be investigated on the nanoscale.<sup>16-18</sup>

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10 Porous GaN has been typically fabricated by (photo)electrochemical and chemical etching  
11 methods,<sup>19-22</sup> giving textured surfaces as a result of pore coalescence and variations in etch rates  
12 for extended etching times. Metal catalysts are also used to initiate growth through either a  
13 vapour-liquid-solid (VLS)<sup>23,24</sup> or vapor-solid-solid (VSS)<sup>25,26</sup> mechanism when using molecular  
14 beam epitaxy (MBE) and chemical vapor deposition (CVD), where the catalyst can influence the  
15 growth, *e.g.* colloidal gold nanoparticles can initiate the growth of GaN nanowires. Additionally,  
16 as the ohmic contact technology to many III-N compounds is now well established<sup>27</sup> the marriage  
17 of seeded growth methods that infer alternative transport properties is an approach that could  
18 allow for new contacts to ternary and quaternary III-nitrides. Alternative techniques that allow  
19 band structure modification while also facilitating the direct growth of GaN, AlN or InN for  
20 example, with resulting low resistivity, ohmic contacts are thus of significant fundamental and  
21 commercial interest.

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24 We produced porous GaN through the direct reaction of metallic Ga with NH<sub>3</sub> in a simple  
25 chemical vapor deposition (CVD) system.<sup>28</sup> Micrometer sized nanoporous GaN particles were  
26 grown directly onto boron nitride (BN) and silicon<sup>29</sup> substrates using this technique without  
27 necessitating any secondary electrochemical or electroless etching, or subsequent chemical  
28 treatment after growth to induce porosity. Furthermore, it is possible to deposit porous GaN  
29 directly onto Si substrates in a single growth step. The development of porous GaN augers well  
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3 for new electronic and optoelectronic devices with improved external quantum efficiencies, the  
4 incorporation of phosphors for LEDs, and high surface area sensing.<sup>30,31</sup>  
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8 Here, we report the successful growth and simultaneous electrical contacting of nanoporous  
9 GaN grown using high workfunction Au- and Pt-coated silicon substrates, through the direct  
10 reaction of Ga and NH<sub>3</sub> in the CVD system. Au and Pt acted both as catalyst for the synthesis of  
11 porous GaN and result in the formation of an intermetallic compound at the GaN-metal interface  
12 that prevents oxidation of the GaN, promotes vapor-solid-solid growth of porous, single crystals,  
13 and in parallel allows for high quality ohmic electrical contacts to the porous layers facilitated by  
14 a significantly reduced Schottky barrier height.  
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## 27 2. EXPERIMENTAL SECTION

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29 **2.1. Synthesis of GaN particles.** Nanoporous GaN microparticles were deposited using a  
30 Chemical Vapor Deposition (CVD) system on Au- and Pt-coated silicon (100) substrates with an  
31 area of 1 cm<sup>2</sup>, using a horizontal single zone split tubular furnace Thermolyne 79300. Figure S1,  
32 Supporting Information, shows a schematic of the experimental setup. The system consists on a  
33 quartz tube inside of which a BN support is placed that holds the Si substrates during the growth  
34 experiments. The BN support has a hole in its centre that allows exposure of the Si substrate to  
35 the Ga source. Gallium metal (99.99%) and ammonia (>99.98%) were used as the Ga and N  
36 sources, respectively. An excess amount of Ga was placed at the bottom of the quartz tube, in  
37 close contact with the temperature-controlling thermocouple. A 20 nm layer of Au or Pt was  
38 deposited on Si substrates using a RF sputtering process (AJA International) at a power of 150 W  
39 and a pressure of 3 mTorr. The coated substrate was placed 2 cm above the Ga source as can be  
40 seen in Figure 1. The quartz tube of the furnace was degassed to a vacuum pressure of  $1 \times 10^{-2}$   
41 Torr, after which NH<sub>3</sub> was introduced through a mass-flow controller at a flow rate of 75 sccm  
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3 and the furnace heated to the reaction temperature of 1203 K at a rate of 100 K min<sup>-1</sup>, while the  
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5 pressure was kept at 15 Torr. The reaction was continued at this temperature and pressure for 60  
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7 min under a constant flow of NH<sub>3</sub>. Growth was halted by cooling to room temperature without  
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9 NH<sub>3</sub> flow, reducing the pressure to 1 × 10<sup>-2</sup> Torr.  
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15 **2.2. Characterization.** The nanoporous GaN microparticles deposited on the Si substrates as a  
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17 porous layer were characterized morphologically using a JEOL JSM 6400 scanning electron  
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19 microscope (SEM). Before observation samples were coated with a thin layer of gold with a Bal-  
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21 Tec SCD004 sputterer.  
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25 Pore shapes, lengths, and propagation directions were analyzed by focused ion beam (FIB)-  
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27 based tomography, *i.e.* time-resolved serial slicing and imaging with a Zeiss 1540 Cross Beam  
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29 microscope (see Supporting Information). This dual beam system is equipped with a FIB column  
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31 with a Ga source and a high resolution field emission electron column. The FIB column stands at  
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33 52° to the electron column and the sample surface is perpendicular to the ion column. The ion  
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35 milling was performed using a 5 pA beam current to minimize surface damage and material  
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37 redeposition.  
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41 X-ray diffraction (XRD) spectra and imaging in  $\theta$ -2 $\theta$  geometry of the as-grown sample were  
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43 made using Cu K $\alpha$  radiation in a Bruker-AXS D8-Discover diffractometer equipped with parallel  
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45 incident beam (Göbel mirror), vertical  $\theta$ - $\theta$  goniometer, XYZ motorized stage and a General Area  
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47 Diffraction Detection System (GADDS) HI-STAR detector with a multiwire proportional counter  
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49 of 30 × 30 cm<sup>2</sup> area and 1024 × 1024 pixel density. Samples were placed directly on the sample  
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51 holder and the area of interest was selected with the aid of a video-laser focusing system. An X-  
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53 ray collimator system allows the analysis of 500  $\mu\text{m}^2$  surface areas. The X-ray diffractometer was  
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55 operated at 40 kV and 40 mA to generate Cu K $\alpha$  radiation. We collected 2D XRD patterns  
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3 covering a range of  $2\theta$  between  $20 - 85^\circ$  at a distance of 15 cm from the sample. The exposure  
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5 time was 120 s per frame. Identification of the crystalline phases was achieved by comparison of  
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7 the XRD diffractogram with the ICDD database using Diffrac<sup>plus</sup> Evaluation software (Bruker  
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9 2007).  
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12 High resolution transmission electron microscopy (HRTEM), convergent beam electron  
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14 diffraction (CBED) were conducted on a JEOL 2100F FEGTEM operating at 200 kV and on a  
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16 JEOL FEM 3000F TEM. Lattice resolution energy dispersive X-ray analysis (EDAX) was  
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18 acquired using EDX Genesis XM 4 system 60 detector.  
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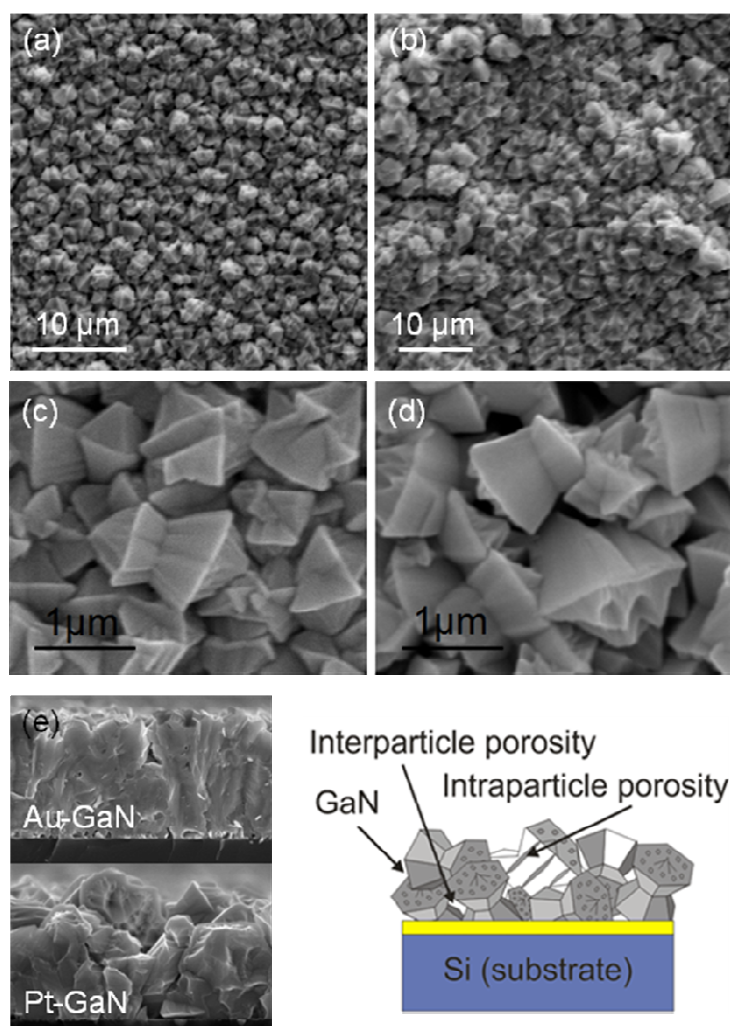
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21 Charge transport measurements through the porous GaN films were conducted using 2- and 4-  
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23 probe measurements using a dc-voltage and an Agilent 34401A Digital Multimeter in a Peltier  
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25 cell, thermostated to 295 K in a Faraday cage. Liquid metal contacts were made using In-Ga  
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27 eutectic blown into a sphere from a gold metallized short borosilicate capillary tube ensuring  
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29 good wetting (several  $\mu\text{m}^2$ ) to the rough top-surface morphology of the porous GaN and avoid  
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31 electrical shorting to the underlying metallized silicon. Measurements were made in 2 probe, 4-  
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33 probe and van der Pauw<sup>32</sup> geometry. Resistivity values were extracted from  $I$ - $V$  curves in the  
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35 high bias regime (series resistance) and also from 4-point probe measurements. Capacitance-  
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37 voltage analysis using gold Schottky contacts to porous GaN was performed by scanning the  
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39 applied potential at a rate of  $10 \text{ mV s}^{-1}$  with a superimposed AC signal with an amplitude of 15  
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41 mV at a frequency of 1 MHz.  
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### 51 3. RESULTS AND DISCUSSIONS

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54 **3.1. Morphological characterization of porous GaN.** The resulting nanoporous GaN  
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56 structures, deposited on the surfaces of Si substrates coated with Au and Pt, were characterized  
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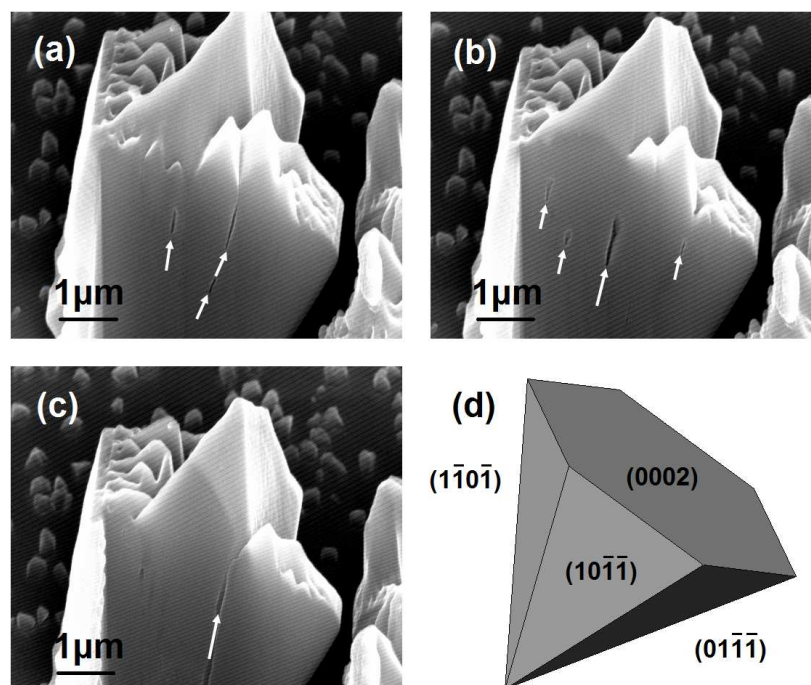


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3 morphologically by SEM. Figures 1(a) and (b) show the typical porous GaN layer morphologies  
4 grown using this approach and in Figs 1(c) and (d), we observe that the porous GaN particles  
5 have a characteristic morphology consisting of faceted hourglass crystals with a mean size of  
6  $\sim 1.5 \mu\text{m}$  end-to-end. The GaN crystals have smooth lateral faces, while pores are observed on  
7 their basal planes, similar to those we observed on BN substrates<sup>28</sup> or Si substrates coated with  
8  $\text{Ni}(\text{NO}_3)_2$ .<sup>29</sup> Crystal growth occurs progressively on the surface with individual crystals ripening  
9 until a layer of porous GaN microparticles covers the surface as a porous layer. The particles  
10 obtained on the Si substrates coated with Pt showed a higher degree of internal porosity, with the  
11 pores aligned along the [0001] direction, than those grown from Au-coated Si substrates.  
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3 **Figure 1.** SEM images of porous GaN particles grown on Si (100) substrates coated with (a,c) 20  
4 nm film of Au and (b,d) 20 nm film of Pt. (e) Cross sectional SEM images of the GaN layers for  
5 each system (bottom left) and schematic representation of a sample of GaN nanoporous particles  
6 grown on a Si substrate coated with Au showing the interparticle and intraparticle porosity of the  
7 GaN layers (bottom right).  
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16 The GaN layers are both microporous and mesoporous. The microporosity stems from the free  
17 space between particles (see Figs 1(c) and (d)), whereas the nanoscale mesoporosity comes from  
18 internal pore features within the particles, confirmed with time-resolved FIB based tomography,  
19 shown in Fig. 2 (a,b,c) together with the simulation of the external morphology of the particle,  
20 shown in Fig. 2 (d). With this technique we analyzed the shape and length of the pores, as well as  
21 their direction of propagation inside of the GaN particles by removing the material, slice-by-slice  
22 using ion-milling, closer to the lateral surfaces of the GaN nanoporous particle. The secondary  
23 electron images recorded concurrently revealed straight pores with lengths similar to the  
24 dimension of the GaN particles. These pores are parallel to the facet direction and do not  
25 intersect nor branch, as can be seen in the video milling sequence in the Supporting Information.  
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27 In some cases the initiation of epitaxial polycrystalline segments within an hour-glass crystal, are  
28 also found as shown in Fig. 2c. The diameters of the pores ranged from 50 to 100 nm, with  
29 negligible variation in diameter with length (non-tapered). From these images and the video  
30 recorded during the tomography (see Supporting Information) performed on different GaN  
31 particles, we conclude that the nanopores in the central part of the GaN particles follow a  
32 orientation parallel to the [0001] crystallographic direction. However, the nanopores found in the  
33 outer portions of the GaN particles are parallel to the lateral faces of these particles.  
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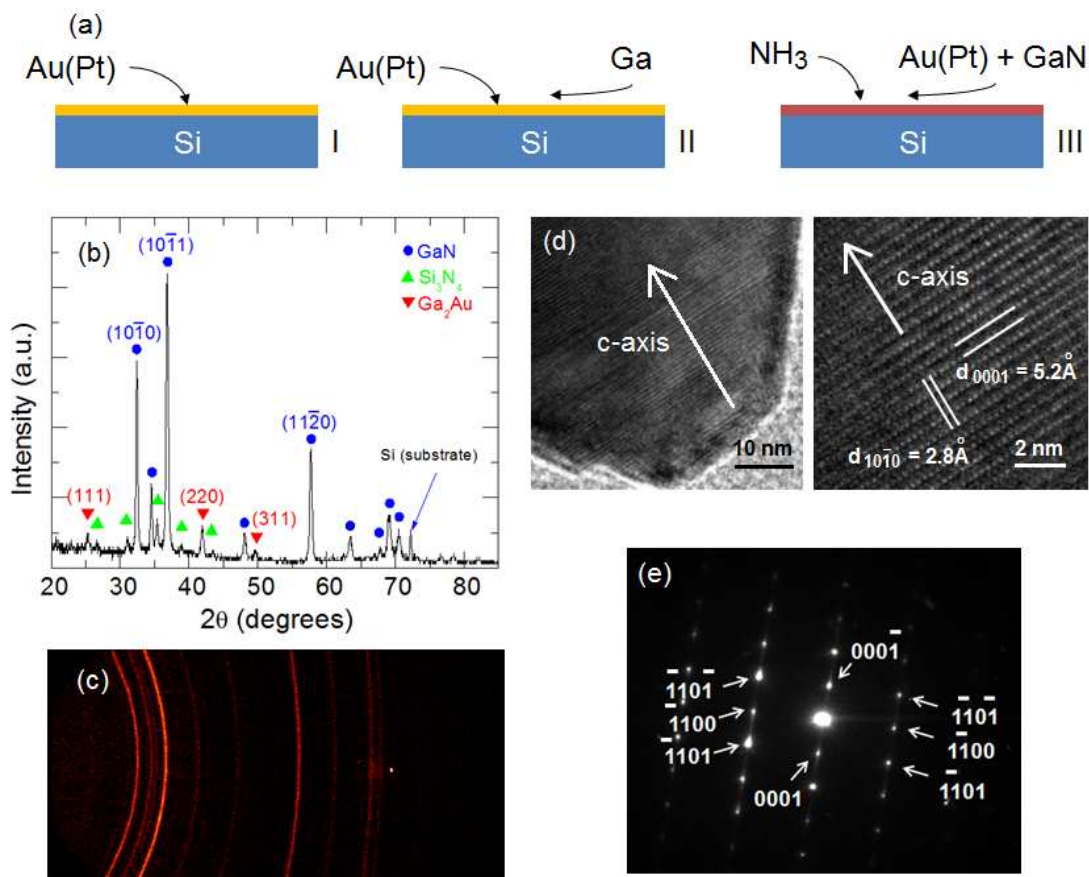


**Figure 2.** FIB tomography acquired with a milling current of 5 pA for a duration of 160 s revealing the GaN intraparticle porosity (a,b,c), and simulation of the morphology of the GaN crystal with terminating crystal planes identified (d).

**3.2. Structural characterization of VSS porous GaN.** The crystalline structure of the porous GaN particles deposited on Si substrates coated with Au and Pt was analysed using X-ray diffraction. The XRD pattern shown in Fig. 3 (b) for GaN grown on Au-coated Si substrates, confirms crystalline wurtzite GaN growth with a predominant diffraction intensity from low-index crystal facets. The regions at which the (400) diffraction peak of Si appears at  $69.131^\circ 2\theta$ , has been excluded from the measurement to avoid intensity saturation. This allows observation of lower intensity reflections that are attributed to crystalline  $\text{Si}_3\text{N}_4$  and a crystalline Au-Ga intermetallic alloy of cubic  $\text{Ga}_2\text{Au}$ . We believe that the  $\text{Si}_3\text{N}_4$  formation is most likely due to reaction between  $\text{NH}_3$  and silicon accelerated by the metallic catalyst.

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3 The formation of the Au-Ga crystalline alloy, which occurs here above the solid-solution  
4 formation temperature of 923 K, confirms intermetallic seeding to form GaN by reaction with  
5 NH<sub>3</sub> through a vapor-solid-solid process. The uniform intensity of the Debye rings (along the  
6 curved ring portions in Fig. 3 (c)) collected for porous GaN confirms that there is no texturing in  
7 the layer of porous crystals (see Fig. 3 (c)).  
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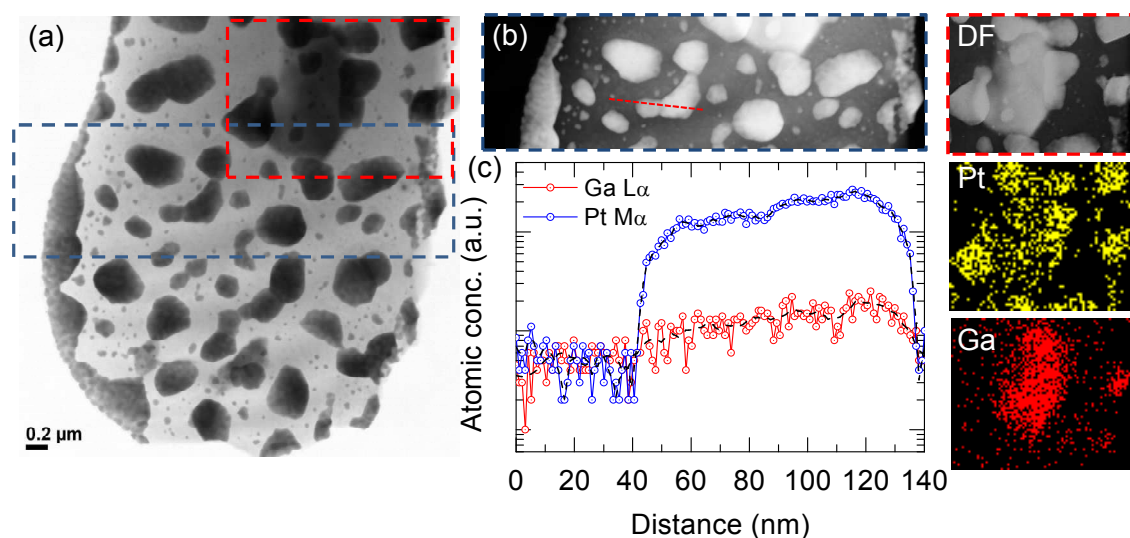
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15 HRTEM measurements were carried out to confirm the crystallinity of the nanoporous GaN  
16 crystals. Figure 3 (d) shows low- and high-magnification HRTEM images of a typical porous  
17 GaN particle. Pores are not directly observable here due to the thickness of the crystal. In the  
18 high-magnification image, the two-dimensional atomic structure of the GaN crystal is resolved.  
19 In this figure we identified two different *d*-spacings of 0.52 and 0.28 nm corresponding to the  
20 (0001) and (10-10) planes of the GaN structure. Figure 3 (e) shows a selected area electron  
21 diffraction (SAED) pattern taken from one of the corners of the GaN porous particle. This  
22 diffraction pattern corresponds to the wurtzite structure of GaN, confirming that the nanoporous  
23 GaN particle is a single crystal. The existence of some (0001) diffraction streaks that generated a  
24 splitting of the diffraction intensity in the SAED patterns, suggest the existence of thin lamellar  
25 defects lying parallel to the (0001) plane<sup>28</sup>; stacking faults along the crystallographic *c*-axis can  
26 be seen in the HRTEM image in Fig. 3(d). The growth of these GaN nanoporous particles is  
27 assisted by a solid particle through the vapour–solid–solid (VSS) mechanism, the main stages of  
28 which are: the Ga incorporation into the Au or Pt solid phase eutectic, the formation of a Ga-Au  
29 or Ga-Pt alloy, the solubilisation of nitrogen in the Ga-Au(Pt) alloy, and finally the nucleation  
30 and growth of GaN (see Fig. 3 (a)).  
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**Figure 3.** (a) Mechanism of growth of the GaN nanoporous particles through the VSS process. (b) XRD pattern for porous GaN deposited on Au-coated Si(100) showing the formation of crystalline GaN (ICDD 01-073-7289),  $\text{Si}_3\text{N}_4$  (ICDD 03-065-8613) and  $\text{Ga}_2\text{Au}$  alloy (ICDD 01-071-6479). (c) Debye rings recorded with GADDS detector indicating no texturation of the porous GaN layer. (d) HRTEM image shows the presence of a few stacking faults and the two-dimensional atomic structure with  $d$ -spacings for the (0001) and (10-10) planes. (e) SAED zone [11-20] axis pattern.

For Pt seeded VSS grown porous GaN, we examined the surface of the silicon substrate directly underneath the GaN crystals. Figure 4 (a) shows a bright field TEM image of a portion of the silicon substrate where the Pt-Ga seed crystals (dark regions) are found. The seeds have

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3 characteristic faceted morphology and shape and the deposit comprises fused grains. EDX  
4 analysis in Fig. 4 (b) confirms the presence of both Pt and Ga, and while the intensity of Pt is  
5 greater as would be expected, the atomic concentration of Ga follows that of Pt, where the  
6 variation stems from increasing seed crystal volume along the line scan. Corresponding mapping  
7 of the intermetallic Pt-Ga seeds in Fig. 4 confirms that not all of the Pt particles contain Ga, *i.e.*  
8 that a proportion of the metallic seeds take up Ga to form the intermetallic, but it should be noted  
9 that the site of interest examined is taken from a region of the substrate between fully grown GaN  
10 crystals. As with the Ga<sub>2</sub>Au seeds, the Pt-Ga seeds are where VSS GaN growth starts, but a  
11 crystalline diffraction pattern is not found for this phase as readily as for Au-seeded GaN.  
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**Figure 4.** (a) Bright field TEM image of the Pt-Ga intermetallic islands formed at the GaN interface and (b) corresponding dark field STEM image with (c) corresponding line profiles of atomic concentration for the Ga L $\alpha$  and Pt M $\alpha$  X-rays. (Right) EDX maps confirming the presence of Pt and Ga in most metallic islands on the silicon surface.

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3 **3.3. Electrical characterization of Pt- and Au-contacted porous GaN.** An important  
4 consideration for porous layers, is that electrically they are sensitive to grain boundary density  
5 and when rough, the sheet and contact resistances ( $\rho_c$ ) are influenced not only by the physical  
6 state of the interface at the contact, but also the geometry. In all cases, the ability to accurately  
7 evaluate the contacts is critical. The standard techniques of linear transmission line  
8 measurements (TLM) and circular TLM (c-TLM) have been established.<sup>12</sup> For porous GaN  
9 specifically, the thickness is determined by the size of the crystals and their assembly on the  
10 surface, which results in a ‘rough’ topology, with a high density of grain boundary scattering  
11 centres. For thin GaN layers with higher (than thick smooth epi-layers) sheet resistance ( $R_s$ ), the  
12 accuracy of the TLM-type approaches becomes an issue. Here, although the layers are quite thick  
13 compared to epi-layers of GaN on LED structures for example, their  $R_s$  values are expected to be  
14 close to that of thin epi-layers. Thus, both TLM and less-geometrically sensitive van der Pauw  
15 measurements were acquired to probe the transport mechanism but also the contact resistivity  
16 and its contribution to the overall resistance, a contribution that decreases with improving  $\rho_c$ .

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36 Figure 5 shows the  $I$ - $V$  curves from the porous GaN catalyzed by Pt (Fig. 5(a)) and also by Au  
37 (Fig. 5(b)), with the second contact placed on the underlying metal, as shown schematically in  
38 Fig. 5. The  $\ln(I)$ - $V$  curves show only slight asymmetry indicative of near-ohmic, weak Schottky  
39 barriers to Pt and Au. Consistently, the conductivity of porous GaN grown from Pt is higher than  
40 that grown from Au. In such cases, there is no detectable presence of any remaining Ga-Pt phases  
41 between the catalyzed GaN and the contact metal. The  $I$ - $V$  curve of porous GaN-Pt in Fig. 5c  
42 shows the low-bias non-linearity consistent with such a weak Schottky barrier. Both contacts fit  
43 with thermionic emission theory, acknowledging a near potential-independent high ideality factor  
44 for near-ohmic barriers. In any diode, a number of transport mechanisms play a role, including  
45 diffusion and tunneling currents in addition to thermionic emission. At room temperature, the  
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3 effective linearity of the  $I$ - $V$  response measured for porous GaN to high work function metals,  
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5 with an intermetallic seed layer between the metal and GaN is maintained at high bias. Since the  
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7 ideality factor does not change due to near-ohmic response, the differential resistance and series  
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9 resistance values are quite similar, as will be shown below. The Schottky barrier height (SBH)  
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11 can still be estimated from  
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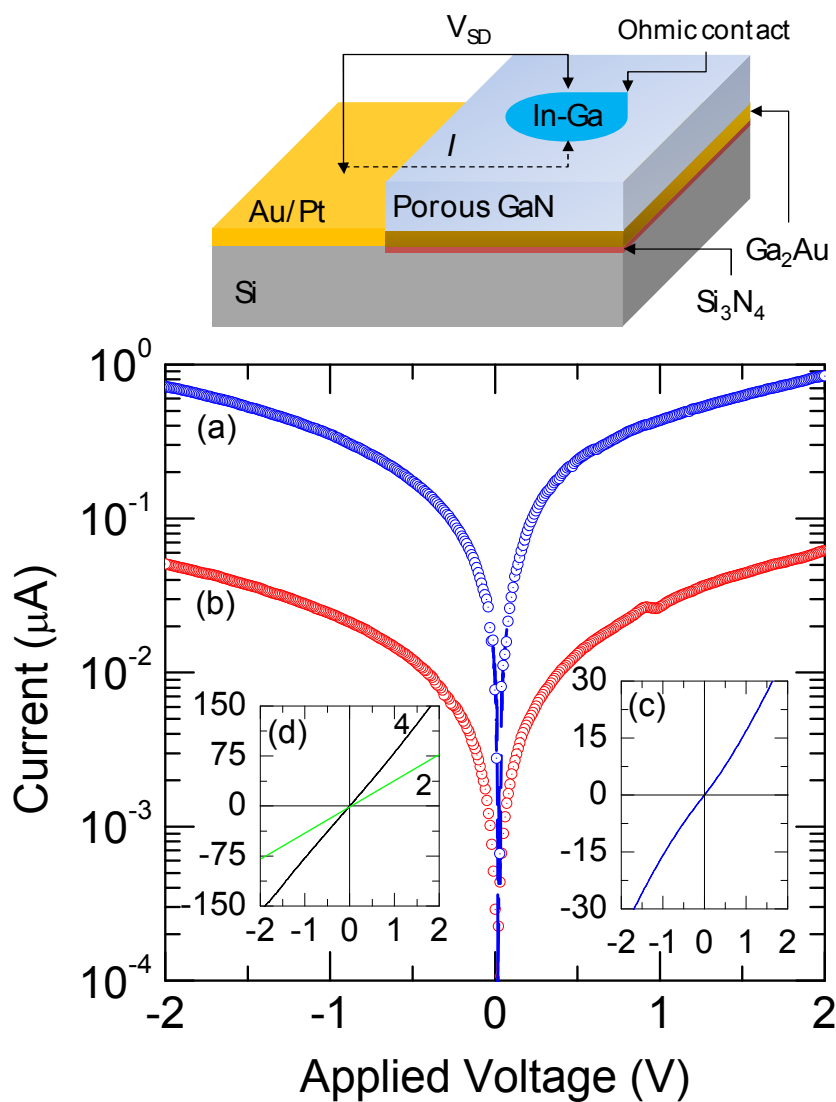
$$I = I_0 \left[ \exp\left(\frac{qV - IR_s}{kT}\right) - 1 \right] \quad (1)$$

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27 where  $I_0 = AA^{**}T^2 \exp(-q\phi_{B,n}^0/kT)^{33}$  where  $A^{**}$  is the effective Richardson constant. The  
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29 estimated SBHs using the theoretical value for the effective Richardson constant ( $26.4 \text{ A cm}^{-2} \text{ K}^{-2}$ )  
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31 for Pt and Au contacted porous GaN are 0.66 eV and 0.53 eV, respectively.  
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34 Effective ohmic contacts can form with n-type GaN suggesting the grain boundary scattering or  
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36 resistivity dominates transport through an alloyed interface that promotes ohmic transport in a far  
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38 from ideal diode arrangement where current flow is through the contact. Two terminal transport  
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40 measurements (Fig. 5d) acquired between the In-Ga ohmic contacts showed perfect ohmicity.  
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42 Corresponding 4-probe analysis gives sheet resistances for porous GaN films in the range 4.3-4.9  
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44  $\text{k}\Omega/\square$ . The van der Pauw measurements confirm these values independent of contact area and  
45  
46 effective geometry on rough surfaces. Additionally, it is important to note that deposited Pt (and  
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48 Au) form coarsened NP distributions after the growth of GaN, due primarily to temperature-  
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50 mediated coalescence and ripening. For electrical measurements, particle distributions confirm  
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52 that both nearest-neighbor distances and overall distribution of various non-spherical particles  
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prevent the formation of a percolating conduction layer beneath the GaN; the electrical characterization is of the porous GaN polycrystalline layer.



**Figure 5.** (Top) Schematic representation of the contacted porous GaN layer. (Bottom)  $\ln(I)$ - $V$  curves for porous GaN grown from (a) Pt and (b) Au. (c)  $I$ - $V$  curve for the porous GaN grown directly from Pt and (d)  $I$ - $V$  curves from 2- and 4-probe measurements using In-Ga ohmic contacts to porous GaN.

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3 Contact resistivities were determined with variable inter-contact separation using the  
4 transmission line measurement (TLM) approach. For the contact resistivity of the rough, faceted  
5 top surface we assume that the semiconductor sheet resistance underneath the contacts remains  
6 unchanged. This is reasonable since no alloyed contacts (referring to the drain contact, not the  
7 interfacial metal-GaN layer) are used which is known to affect sheet resistance.<sup>34</sup> In spite of higher  
8 porosity from Pt-grown porous GaN, low contact resistivities between  $2.2 - 4.1 \times 10^{-4} \Omega \text{ cm}^2$  for  
9 Pt-catalyzed n-GaN and  $5.9 - 8.8 \times 10^{-4} \Omega \text{ cm}^2$  from Au-mediated porous n-GaN layers are  
10 found. Current flow from the porous GaN to the metal is assumed to flow horizontally through  
11 the intermetallic seed layer at the GaN interface and collected at the Au or Pt metallized silicon.  
12 Leakage currents from the slightly more resistive intermetallic seed layers are prevented by the  
13 formation of a crystalline dielectric  $\text{Si}_3\text{N}_4$  layer. This approach is valid so long as the injection of  
14 current across the contact is uniform. The current spreading length, which is a measure of the  
15 effective length over which current is injected into the porous GaN layer is given by  $L_S =$   
16  $\sqrt{(\rho_c/R_S)}$ , and holds for epi-layer systems with two ohmic contacts. From a TLM measurement,  
17 we find that the contribution from the contacts to the overall series resistance between them  
18 scales with  $\sqrt{\rho_c}$  as would be expected from a double ohmic contact system, in spite of high  
19 workfunction metals contacting a rough, n-type GaN layer. The accuracy of  $\rho_c$  is limited by its  
20 relative value compared to the total inter-contact resistance; lower  $\rho_c$  relate to smaller  
21 contributions and increased errors in its determination from TLM measurements and the  
22 geometry of wetting liquid metal contacts to a rough, faceted porous GaN layer, which is  
23 unavoidable. Definitive non-linearity in the  $I-V$  response and also variations in site-to-site  
24 measurement can also contribute to these errors. Here, as the GaN is unintentionally n-type and  
25 consequently has a more uniform doping profile as a function of distance that corresponding p-

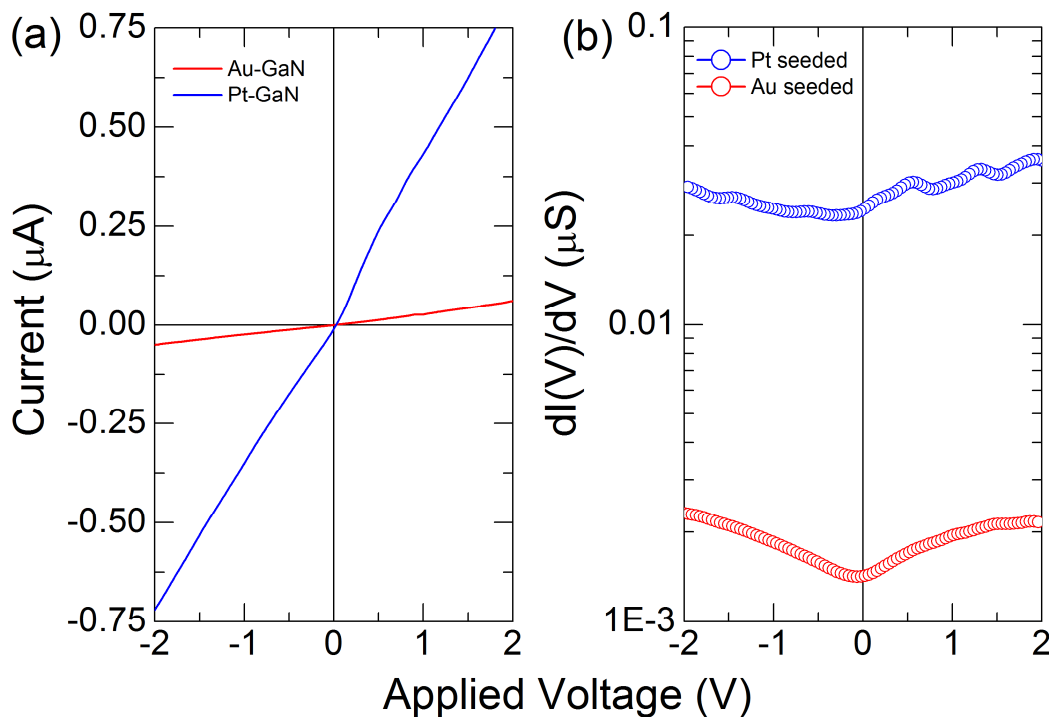
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3 type layers which require temperature-mediated activation, site-to-site variations were found to  
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5 be minimal and varied by ~0.6%.  
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8 Compared to the  $R_s$  values, it is clear that an effective ohmic contact is formed and sheet and  
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10 series resistances through the GaN layer are dominated by the layer structure. The overall series  
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12 resistance,  $R$  to which the sheet and contact resistivities contribute can also be determined from  
13  
14 the thermionic emission theory described above. In the presence of the intermetallic contact, the  
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16 transport is effective ohmic. The series resistance can also be obtained from the differential  
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18 conductance through its proportionality to the current according to  
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$$\frac{dI}{dV} = \left( R_s + \frac{kT}{q} \left[ \frac{1/I_0}{I/I_0 - 1} \right] \right)^{-1} \quad (2)$$

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27 For the thermionic emission-based transport through the porous n-GaN layer, the reciprocal of  
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29  $dI/dV$  approaches  $R_s$  at the higher currents, provided that the ideality factor remains unchanged,  
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31 which is the case here. The differential resistance is plotted in Fig. 6b. As observable from the  $I$ -  
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33  $V$  curves in Fig. 6a, the response from Pt contact porous GaN is slightly less symmetric and thus  
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35 has a slightly higher Schottky barrier giving very weak rectification with a reverse bias current  
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37 that is potential dependent. From Fig. 6b, we find that the differential conductance curves  
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39 confirm this variation in contact type, where porous GaN grown from a seed layer of Ga<sub>2</sub>Au  
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41 exhibits an essentially horizontal response indicative of a linear  $I$ - $V$  curve; the slope varies for Pt  
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43 seeded contacts consistent with a slight non-linearity in the  $I$ - $V$  response, and also a higher  
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45 overall (by a factor of 10-13) conductance compared to Au-seeded porous n-GaN.  
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**Figure 6.** Room temperature (a)  $I$ - $V$  and (b) differential conductance ( $dI(V)/dV$ ) for Au- and Pt-seeded porous GaN layers.

It is worth noting that the n-type contacts were effectively ohmic as deposited and did not need any post-deposition annealing to induce this effective ohmicity; such linear  $I$ - $V$  behaviour is not found with Au contacts and the intermetallic seed layer interface is critical for removing the transport Schottky barrier. The values match those of MBE grown GaN thin films with Ti/Au alloy contacts after annealing to 973 K<sup>35</sup> are caused by the efficient interface between the metal and the growing porous GaN. Additionally, since annealing at 1173 K is known to initially improve contact resistivities down to  $10^{-6} \Omega \text{ cm}^2$  with ohmic Ti/Al contacts, continued heating at this temperature for more than 40 seconds has been shown to result in a drastic increase in  $\rho_c$ .<sup>35</sup> The present method avoids this by the use of noble metal contacts as catalysts and solid seed layers for the GaN growth, and as electrodes for transport measurements.

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3 Capacitance-voltage analysis was performed by scanning the applied potential at a rate of 10  
4 mV s<sup>-1</sup> with a superimposed AC signal with an amplitude of 15 mV at a frequency of 1 MHz to  
5 determine the capacitance of the porous GaN under depletion conditions. For these porous GaN  
6 layers, this frequency was sufficient to sinusoidally vary the depletion region width without  
7 unwanted contributions to capacitance from the dielectric Si<sub>3</sub>N<sub>4</sub> present at the Ga<sub>2</sub>Au interface.  
8 Gold contacts were made to the porous GaN formed a Schottky contact for the measurement. The  
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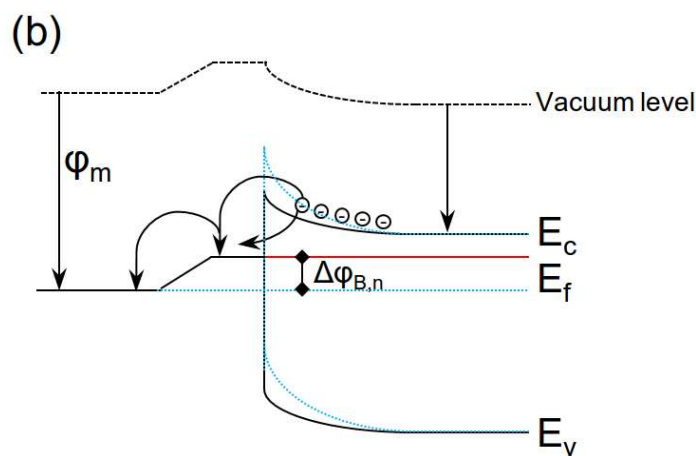
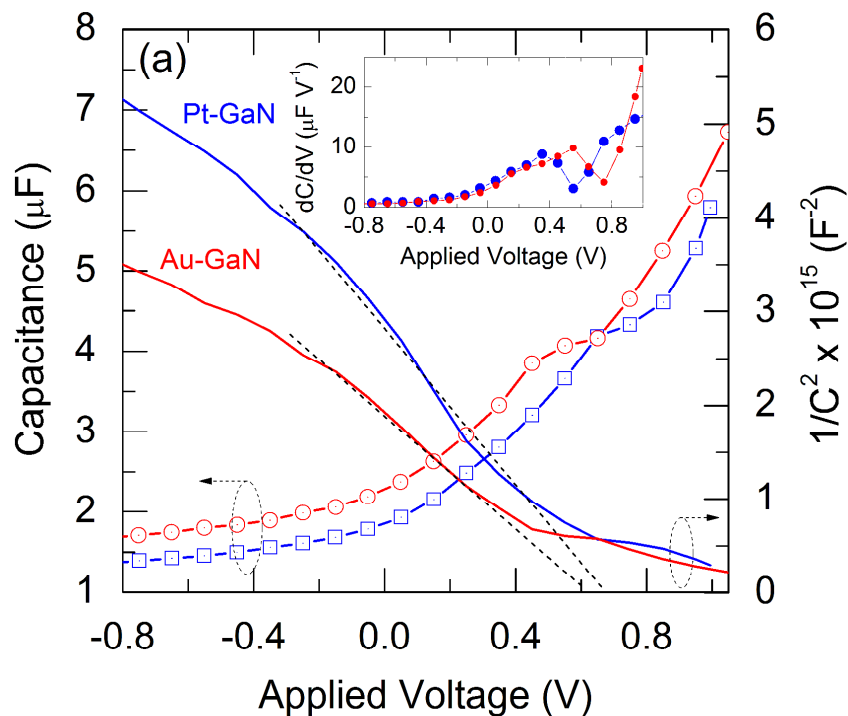
Capacitance-voltage analysis was performed by scanning the applied potential at a rate of 10 mV s<sup>-1</sup> with a superimposed AC signal with an amplitude of 15 mV at a frequency of 1 MHz to determine the capacitance of the porous GaN under depletion conditions. For these porous GaN layers, this frequency was sufficient to sinusoidally vary the depletion region width without unwanted contributions to capacitance from the dielectric Si<sub>3</sub>N<sub>4</sub> present at the Ga<sub>2</sub>Au interface. Gold contacts were made to the porous GaN formed a Schottky contact for the measurement. The 1/C<sup>2</sup>-V analysis in the framework of the Mott-Schottky model, shown in Fig. 7(a), confirms an unintentional n-type GaN with a donor concentration  $N_D$  given by the slope  $N_D = 2C^2V/q\epsilon\epsilon_0$  corresponding to a net impurity concentration<sup>36</sup> in porous GaN of  $n = 1.6 \times 10^{16} \text{ cm}^{-3}$  using a dielectric constant  $\epsilon = 8.9$  for GaN. These low values for unintentionally doped n-GaN give a corresponding SBH from

$$\varphi_{B,n}^0 = eV_{bi} + eV_n + kT \quad (3)$$

where  $eV_{bi}$  is the barrier height from the voltage intercept and  $eV_n = E_{C,n} - E_F$ , of  $0.78 \pm 0.1$  eV and  $0.62 \pm 0.1$  eV for Pt-GaN and Au-GaN respectively. Minima in differential capacitance indicating transition beyond depletion conditions are also found close to the respective values for the built-in potential of these Schottky junctions. These values are lower than standard epi-layer of n-GaN, even when accounting for image force lowering of the barrier height in this case. The Fermi level energy with respect to the Pt and Au workfunction is markedly reduced compared to standard values owing to the interfacial alloy<sup>38</sup> whose work function is less than the respective noble metal, giving lower Schottky barriers to carrier transport through the high grain-boundary

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3 density GaN layer. This is also reflected in the carrier mobilities, which for a doping density of  
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5 effectively  $\sim 10^{16} \text{ cm}^{-3}$ , an average electronic mobility of  $\sim 208 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is determined.  
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8 A plausible band structure for the interfacial intermetallic contact is also shown in Fig. 7(b),  
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10 which shows the presence of the  $\text{Ga}_2\text{Au}$  interface, with its lower workfunction, between the Au  
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12 and GaN (a similar situation can be drawn when using Pt rather than Au). With forward bias,  
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14 electrons can easily overcome the significantly reduced barriers, by thermionic-field emission to  
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16 inject into the Au or Pt from the intermetallic. When the bias becomes negative, holes can tunnel  
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18 through the Au/intermetallic interface barrier and inject into the notch to recombine with  
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20 electrons. The contact resistance is markedly reduced as it provides a recombination center for  
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22 carriers giving a linear  $I$ - $V$  response.  
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**Figure 7.** (a) Interface capacitance and Mott-Schottky ( $1/C^2 - V$ ) profile for Pt and Au catalyzed porous GaN layers. (b) Proposed band structure model for intermetallic interface phase formation acting as the effective ohmic contact. The barrier with (solid line) and without (dashed line) the presence of the intermetallic is shown.

For the low resistance contacts to a porous GaN layer either a low barrier Schottky contact forms with a graded band-gap interface or a tunnel contact is formed. From XRD analysis, a

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3 crystalline  $\text{Si}_3\text{N}_4$  dielectric layer forms when deposition is performed on silicon, just prior to  
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5 continued VSS porous GaN growth and is not likely from N out-diffusion from the GaN. The  
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7 GaN too, is not expected to decompose at 1203 K in  $\text{NH}_3$ ,<sup>38</sup> but the Au and Pt melting points are  
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9 close to this temperature. These metals solidify once the crystalline  $\text{Ga}_2\text{Au}$  solid phase is formed  
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11 as the GaN interface. Oxide growth that would increase the resistivity of the contact is also  
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13 prevented at his growth interface. To examine the reduction in effective barrier height, we  
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15 considered the possibility of the influence of  $\text{Ga}_2\text{O}_3$  formation between the intermetallic and the  
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17 GaN, as is widely known for metal contacts to GaN. The reduction in  $\phi_{0B,n}$  is thus correlated  
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19 with the absence of an insulating oxide, and detailed in the Supporting Information. The variance  
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21 in  $V_{fb}$  from the C-V measurements, as observed in many metal/GaN systems, suggests Fermi-  
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23 level pinning is not prevalent and thus we do not consider surface state-mediated conduction or  
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25 gap states to play a major role in effective ohmicity.  
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31 On Pt and Au however, we confirm an intermetallic  $\text{Ga}_2\text{Au}$  phase typical of VSS growth  
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33 process which suggests a band structure that promotes transport by lowering the Schottky barrier  
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35 by acting as a low barrier, ohmic contact to the GaN, rather than forming a definitive tunnel  
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37 contact which shows ohmicity over a small potential range. In such a case, negative differential  
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39 resistance caused by carrier effective mass increases and reduction in mobility, is prevented. The  
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41 intermetallic formation at the interface that allows the growth of the GaN effectively acts as an  
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43 intermetallic ohmic contact at the semiconductor interface, and the method may be extended to  
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45 growing nanoscale III-N materials and alloys using metals that are not typically employed for  
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47 contacting, to give ohmic response.  
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#### 4. CONCLUSIONS

Porous GaN particles have been successfully grown as high surface area layers from Pt- and Au- coated silicon substrates by a vapor-solid-solid process. The particles form as a layer of single-crystal particles with interparticle and intraparticle porosity. Current-voltage and capacitance-voltage measurements show near-ohmic transport through low-doped, polycrystalline (as a layer), porous n-GaN without alloy contacts or low work function metals. Metal-Ga intermetallic alloy formation during vapor-solid-solid growth promotes thermionic emission-based low-resistance ohmic transport through the porous layer and very low contact resistivities are possible to the faceted, rough n-GaN surface. The ability of contacting the GaN using such metals while at the same time facilitating the growth in a high surface area, crystalline porous network, including intraparticle pores, give opportunities for superior diode-based optoelectronics and sensing and also metallic or colloidal quantum dot inclusions to tune broad-band light emission characteristics. The overall method of using intermetallic as Ohmic contacts could also be applied to simultaneously grow and contact nanoscale III-N compounds for optoelectronic devices.

#### ASSOCIATED CONTENT

**Supporting Information.** Document with further details on crystal growth and electrical characterization. Video of FIB analysis of single GaN particle. This material is available free of charge via the Internet at <http://pubs.acs.org>

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38 SYNOPSIS

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41 Porous GaN are produced using high workfunction Au- and Pt-coated silicon substrates through a  
42  
43 chemical vapour deposition method. Au and Pt acted both as catalyst for the synthesis of porous  
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45 GaN and result in the formation of an intermetallic compound at the GaN-Pt(or Au) interface that  
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47 allows high quality ohmic electrical contacts to the porous n-GaN layers.

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53 **Reduced Workfunction Intermetallic Seed Layers Allow Growth of Porous n-GaN and**  
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55 **Low Resistivity, Ohmic Electron Transport**