Magnetization and magnetoresistance of Ni/nanoporous-GaN composites

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Abstract. Multifunctional semiconductors widen the application scope of existing semiconductor devices. Here we study ferromagnetic-semiconductor composites based on nickel and porous-GaN. Nickel-infiltrated and nickel-coated porous GaN structures were fabricated, and their magnetic and magnetotransport properties were subsequently examined. We found that the magnetization of porous-GaN/Ni electrodeposited composites depended on GaN degree of porosity and the amount of deposited nickel and evolves from a relatively isotropic response to a shape-anisotropy controlled magnetic thin-film behaviour. The magnetoresistance of nickel sputter-coated porous-GaN structures was measured at 300 and 200 K. The temperature-dependent measurements suggested that transport in the GaN layers dictated the room temperature current. Nonetheless, depending on sample pore size, the magnetoresistance displayed high (12-fold) out-of-plane/in-plane anisotropy, and significant hysteresis. These results are uncharacteristic of GaN magnetotransport and point towards magneto-piezo-resistive coupling between the nickel and the porous GaN. These results encourage deeper investigation of magnetic nanostructure property tuning and of magnetic property coupling to GaN and similar materials.
Keywords: GaN; nanoporous; magnetic materials; magnetoelectric; magnetoresistance
Submitted to: JPhys Materials
1. Introduction

Direct band-gap, non-centrosymmetric, semiconductors such as those of the III-V and II-VI families are multifunctional materials offering inherent coupling between mechanical, electrical, optical properties and semiconducting functionality [1–10]. In the past two decades a significant effort to introduce magnetic functionality to semiconductors is ongoing, mainly motivated by spintronic and spinoptic applications [11,12], as well as a magnetoelectric motivation: electrically controlled magnetism [13]. While the dominant route to achieve this property coupling is dilute magnetic semiconductors [14–16], challenges in this technology (low Curie temperatures, solubility limitations) brought increasing interest in magnetic/semiconductor composites [17–21]. The importance of GaN as a semiconducting material, makes it attractive for magnetic/semiconductor coupling. Indeed, various magnetic-GaN applications were demonstrated, including spintronic [22], spinoptic [23] and magneto-electro-optical [24,25]. The coupling between magnetic and semiconducting properties and the ability to control it is highly important, and various methods and geometries to realise the composites exist, including epitaxial growth and phase separation [17,20,21], laminate composites [22,24,26], nanostructure coupling [19,23] and templated deposition [18].

Porous III-V semiconductors have interesting mechanical and optical properties [27–29] and they exhibit enhanced piezoelectricity [30–32]. Filling of porous GaN with an optoelectronic perovskite was recently demonstrated [33]. Filling a porous InP with magnetic material was considered as well [18,30]; these studies, however, did not report on magnetic and electric property coupling. In the following, we describe two methods for fabrication of porous GaN and nickel composites - by electrodeposition and sputtering. We studied the magnetic properties of the composite structures and found that the magnetic response was dependent upon the characteristics of the porous layer and amount of deposited nickel, spanning nearly isotropic responses and transition to thin-film like behaviour. We further found evidence for magneto-piezoresistive coupling in some of our samples. Overall, this study demonstrates the synthesis of laminate and infiltrated Ni/GaN composites, the interplay between synthesis process and magnetic properties and the subsequent magnetic control of electronic properties.

2. Materials and Methods

2.1. GaN growth and electrochemical etching

Si-doped GaN (n-type, 2×10^{18} - 2.3×10^{19} cm^{-3}; 1 µm thick) was grown on a low-dislocation GaN pseudo-substrate [34] on sapphire by metal-organic vapor phase epitaxy (MOVPE) and electrochemically porosified. Electrochemical etching was carried out in a two-electrode configuration. The sample was immersed in oxalic acid (0.25M) with the nitride surface of the doped layer exposed and a DC potential was applied between the sample and a platinum counter electrode. In this process, the porosity degree follows
the voltage, the depth follows time and the process as a whole depends upon doping (through the influence on conductivity) [29,35]. The chosen doping level was $1.85 \times 10^{19}$ cm$^{-3}$ and the etching voltage was either 10 or 12 V, see further discussion in Supporting Information S1. In order to reuse the electrochemical sample configuration, the etch duration was controlled such that a part of the n-doped layer was left intact, with the purpose of acting as a working electrode for subsequent nickel electrodeposition (Figure 1).

2.2. Nickel deposition

Two deposition methods were used: electrodeposition to realise Ni-infiltrated GaN, and sputtering to realise Ni-coated GaN. Electrodeposition was carried out in a three electrode configuration [36], using a counter Pt electrode, and Ag/AgCl reference electrode and the sample as a working electrode. A nickel sulfate (NiSO$_4$) and boric acid (H$_3$BO$_3$) solution, pH 4.5, was used. See complete details in Supporting information S2. For the selected working potential (-1 V), the deposition rate was linear with time (after initial current stabilisation). Following deposition, the samples were washed with DI water and dried under nitrogen flow.

DC magnetron sputtering was used to deposit nickel layers onto porous GaN, using a 99.99% pure nickel source (Goodfellow Limited). The experimental conditions used were 30 W, 2.15 Pa. A permanent marker pen was used as a lift-off resist on the sample edges and non-etched top: it prevented deposition on the covered areas, and dissolved in acetone. Three depositions were carried out with nominal thicknesses of 100, 200, 300 nm (at a nominal rate of 3 nm/sec), resulting in films of $87 \pm 8$, $185 \pm 13$, $190 \pm 21$ nm, as measured by Dektak profilometer. Subsequent electron microscopy and magnetization measurements showed that the amount of nickel was in good agreement with the nominal values, despite the discrepancy in the thickest layer’s profilometer reading.

Figure 1 shows a schematic of the samples and fabrication concepts used in this work (as demonstrated by electron microscopy): electrochemical etching of conductive GaN followed by electrodeposition of nickel (using the same apparatus), or sputtering of nickel on top of GaN.

2.3. Electron microscopy

Scanning electron microscopy (SEM) characterization was carried out using a Zeiss Ultra Plus operated at 2.5-4 kV. SEM and energy dispersive X-ray (EDX) spectroscopy measurements were also done on an FEI Nova NanoSEM operated at 5 kV by imaging secondary electrons. The SEM is equipped with a silicon Drift Detector Energy Dispersive X-ray spectrometer. SEM was also performed using a Hitachi TM3030 desktop tabletop instrument at 12 kV.
Figure 1: Sample preparation schematic. A highly doped GaN layer was electrochemically etched to form porous structures. The same configuration was used to electrodeposit nickel within the pores. Depending on the porous layer conductivity, it was found that nickel either formed on top of the sample, or nucleated on the pore walls. Some of the samples were sputter coated with nickel. The inset shows two electrodeposited samples (top) and one sputtered sample (bottom).

2.4. X-ray diffraction

X-ray diffraction (XRD) measurements were carried out using a Rikagu SmartLab 9 kW without sample rotation. The D/tex Ultra detector in 1D mode and the Ge ((220)x2) monochromator was used, and scanning ($\lambda = 1.541\text{Å}$) was done at high resolution (0.01°) steps, from $2\theta = 43 - 53^\circ$, where we expected to detect Ni signals. (200):(111) integrated peak ratios were calculated manually on the background subtracted data, accounting for cases where (200) peak was not detected by the fitting software.

2.5. Magnetic and magnetoresistive characterization

Temperature dependent Vibrating sample magnetometry (VSM) was carried out using a Physical Property Measurement System (PPMS) DynaCool (Quantum Design) VSM option. The maximal DC H field applied was 10 kOe (1 T). The sample was mounted on a quartz holder for in-plane measurements and inside a plastic straw for out-of-plane data. The diamagnetic/paramagnetic contributions of the holders were subtracted from the signal following linear fitting of the saturated regions. No demagnetization correction factor was used.

Temperature dependent magnetotransport measurements were also carried out in a PPMS DynaCool to calculate the magnetoresistance. The field was applied both in-plane and out-of-plane (relative to the sample surface), with a maximum value of 100
kOe (10 T). The resistance between sputtered nickel and the nominally conductive edge of the sample was monitored by measuring the AC voltage response of the device to an AC current source. See further details in Supporting Information S3.

3. Results and discussion

3.1. Nickel deposition and resulting structures

Two degrees of porosity were examined in this work, controlled by the etching bias: 10 and 12 V, with an (SEM based) estimated porosity of 40-60% and 60-80%, and 30-50 nm and 50-100 nm sized pores, correspondingly. Two nickel deposition methods were considered in this work: electrodeposition of 100-500 sec, and sputtering of 100/200/300 nm. A non-porous control sample, where growth was terminated by 200 nm nominally undoped GaN was sputtered as well (sample NP-300). We designate the samples by their etching voltage (10/12), nickel deposition method (ED/SP) and the deposition duration/thickness; e.g. a 12 V etched sample (larger pore process) which underwent electrodeposition for 150 sec is sample 12-ED-150.

Figure 2 shows cross sectional SEM images of several samples, either electrodeposited or sputtered, the visual appearance of the electrodeposited samples and the electrodeposition current profiles. Apart from the expected increased pore size of the 12 V sample (e.g. Figure 2a compared to Figure 2d), the electrodeposited Ni formed strikingly different structures: sample 12-ED-500 showed a combination of infiltrated nickel (Figure 2c bright contrast) and top coverage. Conversely, sample 10-ED-500 showed mostly a thin-film forming on top of the porous GaN, with only a few nickel nanoparticles forming inside the pores (Figure 2a). We attribute this finding to the role of porous layer conductivity: the epitaxial GaN layer was highly doped. A higher-bias etching (12 compared to 10 V) left behind less material, resulting in an overall higher resistivity (and larger pores). We conclude that the 10 V etching process left the surface sufficiently conductive to allow for electrodeposition directly on the surface - facilitating the deposition of a thin film.

On the other hand the 12 V process resulted in the formation of a Ni-infiltrated structure, evident by the absence of a thin-film on top of 12-ED-150 (Figure 2d). Furthermore, SEM-EDX measurements on a 12-ED-100 sample, revealed the presence of nickel throughout the porous layer, although no deposition was visible in the SEM image itself - see Supporting Information Figure S2.3. Nonetheless, we conclude that in the 12 V etched samples the resistivity was still not low enough to render bottom-up electrodeposition. It is also possible that hydrogen bubbles formed (in a competing route to Ni [37]) during electrodeposition prevented the formation of bottom up growth in the porous, confined, space [38]. Both infiltrated and top-cover electrodeposition routes are depicted in Figure 1. The sputtered samples, as expected, show nickel layers with minimal infiltration inside the pores (Figure 2b). Not all samples exhibited well-cleaved surfaces, which made cross-section imaging challenging. We assume that the
thinner porous section in Figure 2c was a result of cleaving the sample prior to the electrodeposition process.

The visual appearance of the samples reflected their preceding processing (Figure 2e): 12 V etched samples, with infiltrated deposition, displayed a matte finish, while the 10-ED-500 sample, with mostly surface deposition, displayed a lustrous finish. The sputtered samples (not shown here) displayed a mirror-like finish. When considering the current recorded during electrodeposition (Figure 2f), it is interesting to compare the two 500 sec samples: 10-ED-500 showed a current maximum around 150 sec, while it did not reach a maximum in 12-ED-500. Supporting Information Figure S2.1 shows control depositions on ITO substrates, which lasted longer than 500 sec and showed the current mostly saturated after 500 sec. We suggest that the porous substrate plays an interesting role in the evolution of the electrodeposition front-line. When considering the conductive, non-porous, ITO substrates, the deposition nucleates at preferential points, then expands until a stable area and cover is achieved and maintained - resulting in a saturated current [37]. The 12-ED-500 sample exhibited similar profiles, however did not reach saturation in 500 sec. This is possibly due to the larger surface area, leading to larger (volume) density of nucleation points for electrodeposition, combined with 3D growth of the nuclei. The 10-ED-500 sample displayed a different trend and reached a relatively fast maximum. A possible explanation is an initial coexistence of surface and pore nucleation and deposition, where as the pores in the surface were covered, deposition within the pores stopped, reducing the effective area for electrodeposition and correspondingly, the current.

Figure 3 shows a series of XRD patterns obtained from the electrodeposited and sputtered samples. Figure 3a,b shows the patterns obtained from the sputtered samples. The dominant crystallite orientation was Ni(111) with an increase of the (111) signal for thicker layers, while no significant (200) signal was observed, except for a broad peak in NP-300. The integrated (200):(111) peak ratio for NP-300 was lower compared to powder diffraction (27:100 Vs. 45:100 for powder). This indicates (111) preference in our sputtering conditions, and an increased (111) preference in the same conditions for the porous samples.

Figure 3c shows the XRD evolution with electrodeposition duration for 12-ED samples. The dominant crystallite orientation was (111) with a clear increase for longer depositions. The (200) peak was hardly visible even for the longest deposition, with a 12:100 integrated peak ratio found. This result is in agreement with previous reports [38, 39], particularly when considering the 4.5 pH used here [38]. Comparing 12-ED-500 and 10-ED-500 (Figure 3d), 10-ED-500 shows a higher (111) peak, and a well defined (200) peak (15:100). As seen above, the nickel in this deposition formed a continuous layer of about 150 nm. Although the 10-SP-200/300 samples were coated by a thicker nickel layer, their (111) peak is weaker and broader. The poor crystallinity was reflected in the magnetization, as seen below. We were unable to identify the source of the intermittent peak at 2\theta = 49°.
Figure 2: Nickel deposition: a-d) Cross-sectional SEM of [a,c,d] electrodeposited and [b] sputtered samples. All scale bars are 200 nm. The dashed red lines indicate the top layer thickness; e) top view optical image of 10 and 12 V etched samples, after electrodeposition. 10-ED-500 had a metallic finish corresponding to [a]; 12-ED-150 did not, corresponding to the picture arising from [d]. The electrodeposited area was about 0.25 cm$^2$; f) current-time profiles obtained during electrodeposition of four samples.

Applying Scherrer’s equation to the fitted peaks [40], without particularly accounting for other sources for peak broadening, we get a lower estimate for the mean crystallite size. The results for the strongest signals are shown in Table 1. A clear distinction emerges when comparing the deposition methods: electrodeposition resulted in 4-8 times larger crystallites compared to sputtering. This was true even for 12-ED-500 sample where deposition was predominantly inside the pores. The results obtained for 10-ED-500 (thin film structure), with a lower estimate of 40 nm, are in good agreement with previous reports on electrodeposited nickel crystallite size in this pH [38,39]. When comparing the infiltrated (12 V) and the thin film (10 V) electrodeposited structures, the latter exhibited larger crystallites, supporting our assumption that the porous structure could limit the growth.

We further compare the residual strain in the nickel crystallites to a d-spacing of 2.037 Å (or 1.764 Å for (200), where appropriate; after ICSD 04-010-6148). Interestingly, nickel deposited on the 12 V samples results in a slightly higher strain compared to the 10 V samples. The sample porosity strongly affects its mechanical properties, and this could explain the different residual strain. Nonetheless, the differences are not large compared to our estimated confidence level. When considering the non-porous sample, comparing 10-SP-300 and NP-300, the main distinction is the absence of (200) signal in the porous sample. (200) crystallites have been suggested as a route to minimize the
elastic energy in predominantly (111) sputtered nickel film, since (200) direction is associated with a significantly smaller Young’s modulus [41]. This is in agreement with the absence of (200) in the (sputtered) porous samples, as the substrate itself allows strain relaxation in the nickel film. We note that the exact values depend upon the choice of reference, however, even with a different reference used (2.034 Å [42] or 2.03 Å [43]) the trends described above persists, and the strains we find are small.

3.2. Magnetization of nickel deposited on porous GaN

The magnetization was characterised by a series of temperature dependent VSM measurements, taken in-plane and out-of-plane, relative to the GaN surface. The temperatures examined were 2, 50, 100, 200 and 300 K, and the maximum external field (at least) 4000 Oe. Supporting Information Figure S3 shows the in-plane and out-of-plane area-normalized magnetization loops recorded at 2 and 300 K. These curves show the main magnetization trends: an in-plane preference was observed for all electrodeposited samples, despite the dominant (111) out-of-plane orientation of the samples, indicating that shape anisotropy dictates the magnetization and not crystalline anisotropy. The in-plane easy-axis trend was less prominent for short electrodeposition times. The sputtered samples exhibited low remanence and high saturation field, which could be related to the poor crystalline properties of the as-deposited films. In
Table 1: The crystalline properties obtained by XRD from samples with noticeable peaks. $L_{\text{min}}$ is a lower estimate for the Ni(111) crystallite size with a 5 nm error estimate, $\bar{S}$ is the measured strain percent, PR is the integrated (200):(111) peak ratio.

| Sample     | $L_{\text{min}}$ [±5 nm] | $\bar{S}$ [±0.05%] | PR [±1%] |
|------------|--------------------------|---------------------|----------|
| 10-ED-500  | ~40                      | -0.08               | 25       |
| 10-ED-500(200) | ~40                  | -0.14               |          |
| 12-ED-500  | ~30                      | 0.06                | 12       |
| 12-SP-100  | ~5                       | 0.19$^b$            |          |
| 10-SP-100  | ~10                      | -0.14$^b$           |          |
| 10-SP-200  | ~5                       | -0.06$^b$           |          |
| 10-SP-300  | ~10                      | -0.17               |          |
| NP-300     | ~10                      | -0.18               | 27       |
| NP-300(200)| ~5                       | -0.6                |          |

$a$ - Powder (200):(111) peak ratio is 42.5%.

$b$ - Low level of confidence due to shallow peak.

addition, the out-of-plane magnetization exhibited near saturation hysteresis, which is in agreement with previous reports regarding room-temperature sputtered nickel films and associated with perpendicular magnetic anisotropy [43]. The low temperature measurements revealed a bias in the sputtered samples magnetization. The 2 and 50 K 10-SP-100 series were found to have a bias of -240 and -20 Oe, correspondingly. Higher temperature series were bias free (up to a few Oe due to finite measurement resolution near zero magnetization). A lower bias field was also found for 10-SP-300 sample (-180,-17), and a significantly lower bias was found for 10-SP-200, the reasons for this discrepancy are unclear. The bias can be explained by exchange interaction with antiferromagnetic NiO, where the oxidation was enabled by the poor crystalline quality of the as-deposited sputtered layers. No measurable bias was found for the electrodeposited samples. The quenching of the bias field at temperatures higher than 50 K is in agreement with reports of reduced Néel temperature in nanoscale NiO [44,45].

Figure 4a shows the saturation magnetization at 300 K as a function of nominal sputtering thickness for the 10-SP-100/200/300 samples and electrodeposition duration for the 12-ED-150/200/500 samples. The sputtered samples showed a clear linear trend, while the electrodeposited samples did not. Sputtering is indeed expected to be a linear process. The non-linearity in the electrodeposition saturation magnetization is reasonable considering the non-linear characteristics of the current profiles (Figure 2f). Furthermore, we could not account for the role of the total electrodeposited area in our experiments, which could add to inter-sample variance.

Figure 4b shows the temperature dependent saturation magnetization per unit area of all the VSM measured samples. When considering the electrodeposited samples, 10-ED-500 is unique such that nickel was deposited as a layer with almost no infiltration. Therefore it can serve as a useful reference for both deposition methods. Looking back
Figure 4: Saturation magnetization: a) at 300 K as a function of deposition process parameter; as a function of temperature for all samples: b) per unit area; c,d) relative to $M_{2K}$ and compared to theoretical Brillouin ($J = 1/2$, blue solid) and Langevin (red dashed) curves with a Curie temperature of 628 K, for the electrodeposited [c] and the sputtered [d] samples (10-ED-500 appears in both for reference).

at Figure 2a, the layer thickness was measured as 155 ± 38 nm. Using 8.908 g/cm$^3$ for nickel density a saturation magnetization of 56.5 emu/g was obtained for the 2 K series - in excellent agreement with expected value for nickel. The high quality of the electrodeposited nickel was also reflected in the XRD measurements as seen above.

10-ED-500 magnetization properties were markedly different compared to the sputtered samples. Figure 2a,b shows that the thin film atop 10-ED-500 was 50% thicker than that of 10-SP-100 (in agreement with the profilometer measurement). However, 10-ED-500 saturation magnetization was more than 100% higher. Correspondingly, the magnetization of nominally 300 nm (10-SP-300) layer was similar to 10-ED-500, although it was about twice the thickness. Saturation magnetization significantly smaller than bulk crystalline material in as-deposited sputtered thin films is well documented [42,46].

When considering the electrodeposited samples, the effect of etching bias (degree of porosity) on the deposition becomes clearer. As mentioned above, we hypothesize that the conductivity of the remainder of the GaN layer had a significant role to play in
determining the characteristics of the deposited nickel - resulting in a layer for smaller pores and higher conductivity (10-ED-500). The lower saturation magnetization per cm$^2$ obtained for 12-ED-500, supports this hypothesis. This is under the assumption that the electrodeposited nickel has similar properties regardless of shape. We cannot offer a definite conclusion as the total electrodeposited area of these samples was not monitored.

Figure 4c,d shows the saturation magnetization normalized to the 2 K value for electrodeposited and sputtered samples, correspondingly. For reference, the Brillouin (with quantum number J=1/2) and Langevin functions with a Curie temperature of 628 K are also shown. The magnetization evolution with temperature was found to lie between the quantum and classical limits, with the data approaching the Langevin function for shorter/thinner depositions. This could be an indication of a transition from thin film to a more isotropic nano-particle magnetization regime [47].

Figure 5 shows the in-plane and out-of-plane coercivity and remanence of the electrodeposited samples for the entire range of temperatures measured. 10-ED-500 demonstrated in-plane easy axis characteristics, with lower in-plane coercivity and higher remanence. The XRD patterns revealed a dominance of (111) oriented growth - which is the magnetocrystalline easy axis for fcc crystals [47]. It also revealed relatively low strains in all samples, and we can conclude that the thin film shape anisotropy dominates the magnetization of 10-ED-500. We compare the properties of 10-ED-500 to similar thin films grown by Boubatra and co-workers [38]. They found higher coercivity values in their films (120-150 Oe compared to 30 Oe here), despite growth in similar conditions, exhibiting similar crystallinity. They attribute the high coercivity to strain in their films. This is in agreement with the low strains we found in our films, due to relaxation enabled by the porous substrate. The in-plane remanence of 10-ED-500 increased with temperature to a value of 0.6 at 300 K. The reasons for that are unclear and require further studies.

The magnetization of infiltrated samples was different compared to the thin film. The coercivity and remanence of 12-ED-150/200 were similar and we present here only 12-ED-150 to improve figure clarity. A clear trend emerged when comparing 12-ED-150/500 and 10-ED-500. Firstly, the infiltrated samples demonstrated diminished anisotropy. This is manifested in the reduction of the in-plane/out-of-plane difference in coercivity and remanence. Furthermore, the out-of-plane saturation field of the infiltrated samples was considerably lower (Supporting Information Figure S3.1). Overall, the results obtained for both 12 V samples are in between the in-plane/out-of-plane results of 10-ED-500. This trend intensifies in 12-ED-150 where the in-plane and out-of-plane remanence were the closest of all samples measured (still with slight in-plane preference), and the coercivity of 12-ED-150 is lower than that of 12-ED-500. In the infiltrated structure several factors are at play, including particle size and packing. The lower coercivity of 12-ED-150 can indicate a reduction of geometrical particle anisotropy. It can also indicate that following initial nucleation, packing density did not significantly
increase with time and that the particles preferentially grew, rather then nucleate (since increased density is associated with reduced coercivity [47]). Nonetheless, the overall increased in-plane preference in 12-ED-500 indicates enhanced interaction between the particles as they increase in size. These results open the possibility of engineering effectively isotropic magnetic thin films layers by controlling the etching and deposition within porous media.

Figure 5: Magnetization properties of electrodeposited samples: a) Coercivity; b) remanence. Closed/open symbols represent IP/OOP loops.

Figure 6 shows the coercivity (disregarding bias) and remanence of the sputtered samples. Only the in-plane coercivity is shown since the out-of-plane remanence was very low (high saturation field) and a near saturation hysteresis was more pronounced than the near-zero hysteresis. Sample 10-SP-200 exhibited somewhat different characteristics compared to 10-SP-100/300, including smaller bias and coercivity at low temperatures. The reasons for these observations remains unclear.

The low crystallinity of the sputtered films resulted in low saturation magnetization and uncharacteristic loops. The in-plane and out-of-plane saturation fields were comparable, and high compared to the electrodeposited films and infiltrated substrate. The coercivity was higher compared to the electrodeposited film, particularly at low temperatures. The films exhibited low remanence, and particularly low values out-of-plane.
3.3. Magnetoresistance of sputtered-Ni/porous-GaN composites

To examine the coupling between the magnetic and semiconducting phases of the composites we measured the magnetoresistance of two sputtered samples. Due to the high doping level of the GaN chosen for porosification in these experiments ($1.85 \times 10^{19}$ cm$^{-3}$) and nickel infiltration, the electrodeposited samples were highly conductive - which directed the focus towards the sputtered samples. Table 2 summarises the magnetotransport measurements of two samples: 10-SP-200 and 12-SP-200. The conductive path was between the top nickel layer and the sample edge (see further details in Supporting Information S4). This forms a complex path including contributions from all components. The measurements were carried out to understand the governing mechanisms.

Figure 7 shows the in-plane (solid lines) and out-of-plane (dashed lines) MR of two samples, measured between a top sputtered nickel layer (190 nm) and a side contact to the conductive GaN layer. The two samples differed in the etching process of 10 and 12 V, corresponding to smaller and larger pores. We note that the applied field maximum here (10 T) is significantly larger than the normal range of observed saturation in MR [46,48,49], as well as magnetostriction [48,50,51], of nickel. This allows examining
Table 2: The MR properties of two samples sputtered with 190 nm nickel. The resistance value, $R_i$, is shown with an estimated accuracy of ±0.05 Ω, unless stated otherwise. The MR value is the resistance change at the maximal field compared to initial, zero-field resistance. The anisotropic MR, $AMR = (R_{OOP} - R_{IP})/R_{IP}$, is calculated at the maximal field.

| Sample   | Temp. [K] | $R_{|H=0}|$ [Ω] | $MR_{max}$ [%] | $AMR_{|H_{max}}$ [%] | Notes |
|----------|-----------|-----------------|----------------|----------------------|-------|
| 10-SP-200| 300       | 62.34           | 1.77           | 0.75                 | a     |
|          | 200       | 203.28          | -0.59          | 0.39                 | b,c   |
|          | 300       | 63.06           | 0.76           | 0.72                 | a     |
|          | 300       | 285.65          | -              | -                    |       |
| 12-SP-200| 200       | 381.5 ±2        | -              | -                    | d     |
|          | 300       | 285 ±3          | -              | -                    |       |

$a$ - Maximal MR found OOP.

$b$ - Maximal (absolute value) MR found IP.

$c$ - OOP MR not monotonic, making AMR non-trivial.

d - IP and OOP responses very similar.

both the low and high field characteristics.

Figure 7a and Figure 7d show the MR of the two samples measured initially at 300 K (RT). Notably, the responses were markedly different, indicating a profound effect of the porous structure on the magnetoresistive properties of the device: 10-SP-200 demonstrated a positive response, while 12-SP-200 a negative response. There are contradicting reports about the sign of the parallel (field and current direction) MR of nickel [46, 49], however, all reports show a decreasing trend with either transverse or parallel field, even when there is an initial rise to yield a positive value - unlike the result shown in Figure 7a. This is an indication that the MR of 10-SP-200 at RT was not dominated by nickel transport, and that possibly, the transport of 12-SP-200 was significantly affected by nickel MR. Navarro-Quezada and coworkers studied the high-field (up to 6 T) MR of phase separated (Ga,Fe)N particles on the surface of GaN [20]. Their measurements on a control GaN sample (no iron) showed a similar parabolic trend to our out-of-plane RT response (without the initial increase), which supports our assumption. The negative response of 12-SP-200, indicating a nickel dominated transport, could result from the larger pores of this sample - allowing deeper penetration of nickel into the porous structure.

To further investigate the MR, we carried out measurements at 200 K and then again at 300 K. 12-SP-200 underwent measurements at considerably higher current in the second and third measurements (from 10 µA in the first measurement to 10 mA in the later measurements; values are for current amplitude). We cannot exclude that Joule heating (6 orders of magnitude higher power) altered the device, e.g., by annealing of the Ni/GaN interface [52, 53] (see Supporting Information Section S3 for more 12-SP-
200 results). Therefore we continue discussing 10-SP-200 alone, which was measured consistently by applying an AC current with an amplitude of 50 µA.

Figure 7b shows the MR of 10-SP-200 measured at 200 K. The zero-field resistance increased roughly four-fold in the transition from RT to 200 K. This would be expected for a sample where conductance is primarily semiconducting and not metallic - thus confirming our hypothesis about dominant GaN conductance at RT. Furthermore, the low field MR was negative, as expected for nickel, indicating that there are parallel current paths in this device. Interestingly, the out-of-plane and in-plane responses were different apart from the low-field negative MR: the out-of-plane response maintained the positive parabolic characteristic, while the in-plane response demonstrated a negative parabolic relation.

Figure 7c shows the MR of 10-SP-200 measured again at RT. The zero-field resistance returns to the previous RT value at the end of the first field cycle, as do the general trends of the out-of-plane and in-plane responses. The MR value is lower compared to the first RT measurement since the initial increase in resistance was no longer exhibited. The anisotropic MR (AMR) value is similar to the first measurement. Furthermore, by the definition used here, the AMR represents the relative difference at maximal field, and does not reflect the considerable difference between the in-plane and out-of-plane MR. The in-plane MR is considerably low, 0.063%, and the out-of-plane/in-plane MR ratio is 12. Such an anisotropic response has not been observed by Navarro-Quezada et al. in their control measurements of GaN without iron - indicating that the nickel layer influenced the MR of our device - even though it was dominated by GaN transport.

Moreover, the curves in the second RT measurement were less symmetric. This is further evident in the low-field region of the out-of-plane response (Figure 7f). The black arrows show the field sweep direction, and the larger blue arrow points to the estimated curve minimum - noticeably away from zero-field. To further examine this point we fitted the positive part of the negative field sweep and the negative part of the positive field sweep to distinct parabolas, as shown in Figure 8. This was driven by the assumption that the minimal resistance value of the two curves would be different if the resistance (while still dominated by the GaN, as established earlier) was indeed coupled to the hysteretic magnetization. The full results of the fitting process are shown in Supporting Information S3. The points of minimal resistance were: -11500 Oe for the negative sweep and -500 Oe for the positive sweep (estimated error of 10%). This finding suggests that the magnetization of the nickel layer plays a part in the MR, verifying our assumption, thereby suggesting magnetostriction coupled to GaN conductance, possibly through piezoresistance [54,55]. In this context, the overall low response could be related to an inefficient strain transfer between a top layer and the porous layer, as well as the low crystalline and magnetic quality of the sputtered layers.

Due to the geometrical complexity of the structures and the exact directional relation between the critical current flow and the applied magnetic fields, the full extent
Figure 7: Magnetoresistance of sputtered (190 nm) nickel/porous-GaN devices, measured between the nickel and a side contact to the remaining doped GaN layer. At each measurement field, an AC current (0.05 mA amplitude for [a-c]) was applied and the voltage measured. a,b,c) in-plane (solid) and out-of-plane (dashed) MR of 10-SP-200 at RT, 200 K and back at RT, correspondingly; d) the MR of 12-SP-200, a sample with larger pores than 10-SP-200; e) schematic of the samples and measurements; f) the low-field region of the out-of-plane response shown in [c]. The black arrows show the field sweep direction and the vertical arrow points to the estimated region of minimal resistance while sweeping from positive to negative - clearly away from zero-field.

of interactions remains unclear. There is also an existing knowledge gap regarding high magnetic field nickel magnetostriction, which has only been studied at cryogenic temperatures [51], to the best of our knowledge. If so, further work is required to explain the full phenomena range exhibited here, in particular the distinctions between out-of-plane and in-plane response, and their full temperature evolution. This would be achieved by clearer device geometry, and additional controls.

4. Summary

We studied the structural and magnetic properties of Ni/porous-GaN composites prepared either by electrodeposition or by sputtering onto the porous surface. Our results indicate a rich magnetic response, intricately dependent on the deposition method, amount of nickel deposited and the porosity (degree, and pore size). In particular, we found that deposition on porous materials is characterised by low strains and dominant (111) out of plane orientation of the deposited nickel. Electrodeposition was found to have good crystallinity without subsequent treatments and allowed for realization of nickel-infiltrated composites. These nickel-infiltrated composites exhibited
low magnetic anisotropy despite their overall thin-film form. The porous surface was found to influence the structure of sputtered films, in the suppression of (200) crystallite formation. Furthermore, we examined the magnetotransport at high field (up to 10 T) of sputtered thin-film samples at 300 and 200 K. The MR exhibited distinct responses depending on the underlying GaN pore size. The sample of smaller pores exhibited positive MR, which rules out metallic conductance through the nickel as the dominant current mechanism - indicating that the resistance is determined by GaN conductance at room temperature. This was further confirmed by the increase of the overall resistance observed at 200 K. The MR at 300 K exhibited high anisotropy and hysteresis which are uncharacteristic to GaN transport. This indicates coupling between nickel magnetism and GaN conductance and we suggest is mediated through their magnetostriction and piezoresistance, correspondingly. These results direct further investigations on the ability to control the magnetic properties of nanostructures and of magnetic/semiconducting material composites to develop new applications coupling these properties.

Data and Supporting Information

The data that support the findings of this study are openly available at http://Supporting information is available on the publisher website.

Acknowledgments

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Evidence of magneto-piezoresistive coupling in Ni/nanoporous-GaN composites

Supplementary Information
Section S1. GaN growth and Etching

Figure S1 shows cross-sectional SEM images of about 1 µm porous GaN etched at different voltages, of differently doped samples. Etching is stronger for higher doping and higher voltages, and the resulting effect is visible to the naked eye, in light reflectance properties.

Figure S1. a) Cross-sectional SEM image showing etching efficiency increased with voltage; b) top-view SEM image showing increased etching with voltage; c) optical images of samples similar to the ones reported, doped $1.85 \times 10^{19}$ cm$^{-3}$ and etched at 10 and 12 V. Taken at different angles, the samples reflect light differently, following the different etching.
Section S2. Nickel electrodeposition

Calibration depositions were made using ITO coated PET. The relation between thickness and deposition voltage was found to be highly non-linear, while it was linear with deposition time. This also reflected in magnetization, where the magnetization vs. the total charge passed in the process also showed a linear trend.

Figure S2.1 Thickness of electrodeposited nickel as vs. voltage (top, for 1800 s), and vs. time (middle, using -1 V). The bottom image shows control current evolution curves.

Figure S2.2 Magnetization vs. electrodeposition charge obtained by integrating over the current.
Figure S2.3 SEM-EDX data obtained from 12-ED-100. No significant distinctions along the sample cross section were found.
Section S3. Magnetization loops

Figure S3.1 shows the magnetization loops measured at 2 and 300 K in-plane and out-of-plane, close to zero field.

Figure S3.1 Low field region magnetization loops.
Figure S3.1 shows the full range magnetization loops measured at 2 and 300 K in-plane and out-of-plane.

Figure S3.2 Full magnetization loops.
Section S4. Magnetoresistance measurements

Figure S4.1 shows the sputtered samples under the bonding stereoscope, as captured by a cellular phone camera. A 4-probe measurement was applied in order to allow very low AC signals to be applied and measured (as the resistance was very low), however the physical connections are in 2-probe, with the current and voltage leads connected to the same pads (the nickel layer and the solder on the sample side). The resistance measured includes therefore contact resistance, which should be very low, if present at all.

Figure S4.1 The 10 V (left) and 12 V (right) etched samples bonded to the PPMS sample holder. Each pad is connected by two bonds as contingency. Figure S4.2 shows the measured MR of 12-SP-200 at 200 K and back at 300 K. Notably, the resistance at 200 K increased as well, however only in about 50% (compared to a 3-fold increase in 10-SP-200). The resistance in the return to 300 K was not similar to the first measurement - an indication that the device has indeed changed, possibly due to the higher current applied. The consistent feature is that there was no obvious distinction between the in-plane and out-of-plane measurements.
Figure S4.2 Magnetoresistance data of 12-SP-200 at 200 K (top) and the second measurement at 300 K (bottom). Out-of-plane data is dashed.

The fitted curves in the main Figure 7 are given by:

\[
R_{\text{right}} = 4.257 \times 10^{-3} H^2 + 9.655 \times 10^{-3} H + 63.02
\]

\[
R_{\text{left}} = 4.188 \times 10^{-3} H^2 + 4.154 \times 10^{-4} H + 62.98
\]

where \( H \) is in \( 10^4 \) Oe and \( R \) in \( \Omega \). The fitting values are obtained by MATLAB’s cftool, with a 95% confidence. We therefore estimate the error of \( H|_{R_{\text{min}}} = (-b/2a) \) as 10% (with \( b \) and \( a \) the 2nd order polynomial coefficients). The R-square values of both fits were > 99.8%.