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Coexisting structural phases in the catalytically driven growth of rock salt GdN

Ali Shaib, Franck Natali, Jay R Chan, Felicia Ullstad, William F Holmes-Hewett, Jackson D Miller, Ben J Ruck and Harry J Trodahl

The MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand

E-mail: franck.natali@vuw.ac.nz

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Abstract

We present a study of polycrystalline thin films of the rock salt rare earth nitride GdN grown on amorphous fused silica at ambient temperature with varying N2 pressure. X-ray diffraction measurements show a strong (111) preferential orientation for all N2 pressure and the signature of a secondary phase of GdN that develops as the N2 pressure decreases. The secondary phase is found to have a smaller lattice parameter than the near-stoichiometric GdN. Raman spectroscopy, electrical and magnetic results support the coexistence of such mixed-phase samples with the lattice distortion originating from nitrogen vacancies. Significantly the magnetic data show an increase of the ferromagnetic onset temperature as the secondary phase develops, without affecting the soft ferromagnetic character of GdN.

Introduction

The last decade has seen an enormous expansion in studies of intrinsic ferromagnetic semiconductors, either 2D dimensional materials or thin films, which has opened a powerful new perspective in materials science and spintronics applications [1–5]. Within this scenario the fourteen mononitrides of the rare-earth (RENs) are of special interest as they are to date the only known series of intrinsic ferromagnetic semiconductors [1]. Most of the RENs are narrow bandgap semiconductors, with strongly contrasting magnetic properties from the coupled spin and orbital moments residing in the rare-earth 4f shells, and Curie temperatures typically below 50–70 K [1]. Equally interesting, but unexpected until recent experimental observations and computational treatments, are (i) the key signature of superconductivity in the ferromagnetic semiconductor samarium nitride (SmN) [6], (ii) nearly triple nodal point topological phase [7] and (iii) Chern insulating state in gadolinium nitride (GdN) [8] opening new avenues of investigations. Within the context of device applications, there has been a particular interest in using the RENs in hybrid structures, i.e. multilayer structures, in conjunction with, for example, conventional semiconductors [9–11], superconductors [12, 13] or topological insulators [14, 15]; the latter spawning the field of superconducting spintronics that could lead to novel cryogenic spin-based applications. To date such devices rely mostly on polycrystalline films, as a low growth temperature is required to avoid degradation of the structures or intermixing between layers.

Gadolinium nitride (GdN), the most studied of the RENs, lies in the center of the series with a purely spin magnetic moment of $7 \mu_B$ in the half-filled 4f shell of Gd$^{3+}$; uniquely within the RENs, there is no orbital contribution from the 4f electrons. Electron transport occurs in the 5d conduction band, with n-type conductivity, primarily due to doping by nitrogen–vacancy ($V_N$) donors. A ferromagnetic 5d–4f exchange interaction ensures that the 5d alignment follows the 4f alignment, thus retaining the strong interplay between magnetism and charge transport [16–18]. In the present letter, we report key aspects of the growth of polycrystalline GdN thin films of importance for the exploitation of the RENs, including preferential growth and the coexistence of two (111)-oriented phases supported by X-ray diffraction measurements. Raman spectroscopy, electrical and magnetic measurements are carried out with results supporting the coexistence of...
such mixed-phase samples. These two phases are representative of regions within the GdN films where nitrogen vacancies are absent/present, and although they share an FCC crystallographic structure, they show contrasting physical properties; one with the ‘classical’ behavior commonly reported in early (20th century) studies, labeled here as GdN-II, apparently associated with a nitrogen-deficient phase. Films grown with a reduced level of nitrogen vacancies ($V_N$) (i.e. at a high $N_2$ partial pressure), which we identify as intrinsic and label GdN-I, show a lattice constant some 1% expanded relative to GdN-II.

One should note that there is a range of experimental lattice parameter values reported in the literature, varying by more than 5%, ranging from 4.85 to 5.12 Å, with most values about 5.00 Å [19–25, 26]. Our results suggest that this is related to the stoichiometry of the GdN film and bulk samples, RENs being prone to $V_N$. So far there has not been an attempt to explore this avenue, with most reports focusing on the $V_N$-dependent magnetic and conductive properties. Early results in the 1960–1970s established the fcc NaCl structure of GdN with lattice constants marginally smaller than 5 Å [25, 27, 28], while most REN samples at this time showed conductivities suggesting $V_N$ concentration up to few % [1, 29]. More recently, epitaxial thin films of GdN return similar lattice parameters, but relatively high $V_N$ concentrations remain a problem. In view of the epitaxial growth temperature, typically above 500 °C, and the small $V_N$ formation energy [20, 22, 30], it is no surprise that the epitaxial films show a high conductivity. Interestingly the films grown at ambient temperature, i.e. polycrystalline films, show a clear tendency to have lattice parameters greater than 5 Å, suggesting a competing GdN phase that might be influenced by controlling the $N_2$ growth partial pressure. Note that the signatures of a second phase, corresponding to our GdN-II, has been reported by Senapati et al with an antiferromagnetic behaviour [31, 32]. Our present study would rather support that GdN-II is ferromagnetic, but with an enhanced Curie temperature in comparison with stoichiometric GdN-I.

**Experimental**

**Section**

Polycrystalline thin films of GdN were deposited on fused silica substrates at ambient temperature in a molecular beam epitaxy system with a base pressure of $10^{-9}$ mbar. Amorphous substrates were chosen to minimise the effect of preferential nucleation and strain that would arise on a crystalline substrate. The substrates were outgassed at 600 °C for two hours before deposition. Gd metal was evaporated using an electron beam in the presence of a molecular nitrogen ($N_2$) partial pressure ranging from $1 \times 10^{-5}$ to $3 \times 10^{-4}$ mbar. It is important to point out that the molecular nitrogen reacts spontaneously with Gd at the surface to form a GdN layer, even in the absence of activated $N_2$ [33]. This remarkable catalytic activity of the rare earth ions has been demonstrated for most rare-earth elements, and implies a catalytically driven growth process of GdN. The film deposition rate was 300 Å/min. This remarkable catalytic activity of the rare earth ions has been demonstrated for most rare-earth elements, and implies a catalytically driven growth process of GdN. The film deposition rate was 300–350 nm/h and the film thicknesses were ~300 nm. A GaN cap is deposited at ambient temperature on top of the GdN layer to passivate the sample for ex situ measurements. The film thicknesses were measured using scanning electron microscopy (SEM) and symmetric 20–2θ X-ray diffraction (XRD) scans were used to characterize the out-of-plane crystalline structure and texture of the films. The XRD machine used to collect the data utilizes a Cu(Kα) source and emits beams with a wavelength $\lambda = 1.5406$ Å. The XRD peaks for GdN were indexed using ICDD card PDF 04-003-4910 (ICDD, 2020) [34]. Raman spectra were gathered at ambient temperature with a Jobin-Yvon LabRam HR, using a 514.5 nm (2.41 eV) Ar + laser line (0.5 mW). Samples used for SEM measurements were grown on conductive silicon. Room temperature resistivity measurements were performed using a van der Pauw geometry with silver conductive paint contacts, and the magnetic properties of the films were investigated down to 4 K using a superconducting quantum interference device magnetometer.

Diamagnetic fused silica substrates were used for the growth. Correction to the inverse susceptibility due to any contamination contribution (diamagnetic substrate, sample holder...) was applied by modifying the Curie-Weiss law using the following formula:

$$
\chi = \frac{c}{T - T_c} - \left(\frac{M}{H}\right)
$$

where $\chi$ is the magnetic susceptibility of GdN in paramagnetic phase, $c$ is the Curie constant, $T$ is the temperature, $T_c$ is the ferromagnetic transition temperature, $H$ is the applied magnetic field, and $M$ is magnetization contribution of any contaminations (originating from the substrate, or otherwise). $c$, $T_c$, and $M$ are fitting parameters obtained by fitting the inverse susceptibility of the films as a function of the temperature at the paramagnetic phase.
Results and discussion

The XRD diffractograms of samples grown at different N\textsubscript{2} pressure are shown in figure 1(a), with clear signatures of GdN in all samples. The films are polycrystalline with a rock salt structure with data clearly showing that the N\textsubscript{2} pressure is playing an important role in determining the crystal orientation of the GdN films. A strong self-texture, a preferential orientation, along the (111) direction can be clearly observed for all samples grown, while other orientations, (200, 220, and 311) develop with contributions that intensify as the N\textsubscript{2} pressure decreases. Note that all crystallographic orientations are present in the films but grow at various rates with the (111) preferred orientation developing gradually with film thicknesses\cite{35}. Rock-salt materials are known to have the propensity to grow along the (111) close-packed plane rather than the expected (002) when growth conditions favor a competitive columnar growth where large surface diffusion and faceted grains are present\cite{36–40}. Such a complex process is further amplified in our case of study as active-nitrogen species are provided from catalytically-driven growth of the films requiring active Gd ad-atoms sites to break the strong N\textsubscript{2} bonds. The (111) preferential orientation may also be favored by surfaces exhibiting higher catalytic activity, further enhanced under high N\textsubscript{2} pressure\cite{41,42}.

A closer look at the (111) peak reveals a gradual asymmetry developing with decreasing N\textsubscript{2} growth pressure, suggesting a second phase, GdN-II, coexisting with the intrinsic GdN-I phase. Note that no GdN-II phase is found for samples grown at high N\textsubscript{2} pressure, with the (111) intrinsic GdN-I peak being fitted with a single Lorentzian function centered at 30.8° (figure 1(b)). The corresponding lattice parameter for the sample grown at the highest N\textsubscript{2} pressure, the closest to stochiometric GdN, is a\textsubscript{GdN-I} = 5.024 Å. For samples grown at lower N\textsubscript{2} pressure the (111) peak is deconvoluted in two Lorentzian functions to take into account the two phases. Interestingly enough, a good fitting can be obtained by keeping the intrinsic GdN-I peak position constant and allowing the GdN-II peak to move towards higher angles with decreasing the N\textsubscript{2} growth pressure (figure 1(c)). The GdN-II phase becomes predominant as the N\textsubscript{2} pressure decreases, and appears only for N\textsubscript{2} pressure lower than 8 × 10\textsuperscript{-5} mbar. The lattice parameter of the GdN-II phase for the sample grown at the lowest pressure (1 × 10\textsuperscript{-5} mbar) is a\textsubscript{GdN-II} = 4.971 Å, as stated above corresponding to the literature values for N-deficient samples. Significantly such secondary phase has already been reported in the literature, at a lower angle that our GdN-I, and was associated to V\textsubscript{N} distorting locally the GdN lattice\cite{31,32}. It is worth pointing out that a full assessment of the local distortion/average displacement of the atoms of the lattice and the type of bond
rupturing/rearrangement in metal nitrides, such as TiN, NbN, VN has been investigated, but requires highly
deficient nitrogen, i.e. substoichiometric, samples; much more than the few percent of VN present in our GdN films [41, 43, 44].

We have used Raman spectroscopy (figure 2(a)) for the indirect structural information it supplies. Central to its use is that in regard is that no atoms at a centre of inversion symmetry can participate in a Raman active mode, so that the inversion symmetry at both anion and cation sites in a NaCl structure ensures that there are no first-order Raman signals from such a structure. Nonetheless there are Raman lines in the RENs, which have been suggested as arising from the loss of inversion symmetry for ions in the vicinity of VN [45]. The Raman lines, in the 500–550 cm\(^{-1}\) range, are at only ~5% lower in frequency than the TO phonon mode expected at the L point, a mode that has also been assigned as arising from VN activation in rock-salt ScN [44]. It is significant that the corresponding zone-centre mode is also found 5% lower than predicted [46, 47], and indeed such low-level disagreement is common for the LDA models used to predict vibration-mode frequencies.

Within this scenario the results of figure 2(a) are surprising, for the Raman signal is found to be substantially stronger in the films with the smallest VN concentration. The immediate suggestion is that the line is in fact not associated with nitrogen vacancies at all, rather it is rendered Raman active by a structural change that draws the predicted L-point vibration to the zone centre, where it could become Raman active. The simplest such change would be the formation of a superlattice that doubles the unit cell in the predicted L-point vibration to the zone centre, where it could become Raman active. The first structural information it supplies. Central to its use is that in regard is that no atoms at a centre of inversion symmetry can participate in a Raman active mode, so that the inversion symmetry at both anion and cation sites in a NaCl structure ensures that there are no first-order Raman signals from such a structure. Nonetheless there are Raman lines in the RENs, which have been suggested as arising from the loss of inversion symmetry for ions in the vicinity of VN [45]. The Raman lines, in the 500–550 cm\(^{-1}\) range, are at only ~5% lower in frequency than the TO phonon mode expected at the L point, a mode that has also been assigned as arising from VN activation in rock-salt ScN [44]. It is significant that the corresponding zone-centre mode is also found 5% lower than predicted [46, 47], and indeed such low-level disagreement is common for the LDA models used to predict vibration-mode frequencies.

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To investigate the samples further, the room temperature electrical resistivity of the GdN samples is plotted as a function of the N\(_2\) growth pressure figure 2(b). The resistivity decreases by over 4 orders of magnitude under reduced N\(_2\) growth pressure, implying immediately an increase of the VN concentration with the decrease of the N\(_2\) pressure. It has been reported that the VN density can be tuned by the growth conditions such as the N\(_2\) pressure or compensated doping, but it has remained difficult to reduce the VN density much below the 1% level, explaining the moderate resistivity for the GdN samples grown at high N\(_2\) pressure [22, 30, 31, 48, 49].

The room temperature Hall effect for the most conductive sample, i.e. grown at the lowest N\(_2\) pressure (1 × 10\(^{-5}\) mbar), shows an n-type conduction with a carrier concentration of 3 × 10\(^{20}\) cm\(^{-3}\). The following formula is used to calculate the VN level in the film:

\[
VN = \frac{n(V)}{n(N)}
\]

where \(n(V)\) is the number of vacant nitrogen sites/cm\(^3\), and \(n(N)\) is the total number of nitrogen sites/cm\(^3\). We obtain \(n(V)\) from the carrier concentration, assuming that each VN provides the films with as many as three electrons per VN; \(n(N)\) is calculated using the molar density of stoichiometric GdN. This suggests a vacancy density of the order of ~0.3%. This again highlights the extreme sensitivity of the conductance to the growth conditions.

We turn next to the magnetic measurements in figure 3 showing that our films are all ferromagnetic at low temperature, though with differences among their detailed magnetic response. The temperature-dependent inverse susceptibility (not shown) from the field-cooled (FC) magnetisation measurements (figure 3(a)) yield Curie temperatures (\(T_C\)) extracted from the paramagnetic regime using the Curie-Weiss law return Curie...
temperatures \( (T_c) \) that rise from \( \sim 50 \) K in near-stoichiometric films to approach 100 K in the most severely nitrogen deficient films, as has been reported \([16, 48]\). A signature of a varying \( T_c \) is also seen clearly in figure 3(a), where there is a clear shoulder in the magnetization at about 50–55 K developing as the \( N_2 \) growth pressure is decreased. At a growth pressure of \( 3 \times 10^{-4} \) mbar, the sample appears to transform homogeneously in the ferromagnetic phase at 72 K, with no 50 K shoulder. Such behavior has been related to a magnetic polarons scenario \([16]\). We draw these results together by plotting the onset of ferromagnetism as a function of the \( N_2 \) pressure (figure 3(b)). There is a clear \( N_2 \)-pressure effect on the onset of ferromagnetism supporting that an increase of \( V_{N_2} \) results in an increase of \( T_c \). Figure 3(c) shows also that the coercive field does not change significantly with the \( N_2 \) pressure suggesting that the condensation of a secondary GdN phase does not change the soft ferromagnetic character of GdN. This soft ferromagnetic character is shown with better clarity by the lack of any significant variation in the coercive field values of films grown across the total \( N_2 \) pressure range used for the study and measured at 5 K, as shown in figure 4(b). Finally, we compare the hysteresis loops for 2 GdN films grown at an order of magnitude different \( N_2 \) growth pressure (\( 3 \times 10^{-5} \) mbar and \( 3 \times 10^{-4} \) mbar) present in figure 4(a). The absence of any significant change in the coercive field values measured at temperatures up to 50 K confirms the absence of an antiferromagnetic behavior of the GdN-II phase. This disagrees with previous reports suggesting that the GdN-II phase is antiferromagnetic \([31, 32]\), resulting in a ferromagnetic–antiferromagnetic system enhancing the coercivity \([50, 51]\).

Figure 3. (a) Normalised field–cooled temperature dependent magnetization for GdN thin films grown under \( N_2 \) pressure of \( 5 \times 10^{-5}, 8 \times 10^{-5} \) and \( 3 \times 10^{-4} \) mbar. The applied field is 200 Oe. (b) Curie temperature (\( T_c \)) as a function of \( N_2 \) growth pressure. Dashed line is a guide for the eye. (c) Coercive field as a function of the temperature for GdN samples grown under \( N_2 \) growth pressure ranging from \( 1 \times 10^{-5} \) to \( 3 \times 10^{-4} \) mbar.
In conclusion, we have studied the correlation between the structural, electrical, and magnetic properties of the catalytically driven growth of GdN. XRD measurements show the signature of a secondary phase of GdN that develops as the N$_2$ pressure decreases, which has a smaller lattice parameter than the near-stoichiometric GdN. Supported by Raman and electrical results, we associate this phase to N-deficient regions. Simultaneously, we observe an increase of the Curie temperature with the increase of the N-deficient regions, i.e. lower N$_2$ growth pressure, with results consistent with an inhomogeneous transition from ferromagnetic active N-deficient regions.

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Notes

The authors declare no competing financial interest.

ORCID iDs

Franck Natali  https://orcid.org/0000-0001-5407-1929
Jay R Chan  https://orcid.org/0000-0001-6548-1093

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