Semiconducting ground state of GdN thin films

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We report the growth of GdN thin films and a study of their structure and magnetic and conducting properties. It is demonstrated that they are semiconducting at ambient temperature with nitrogen vacancies the dominant dopant. The films are ferromagnetic below 68 K, and a significant narrowing of the band gap is signaled by more than a doubling of its conductivity. The conductivity in the low-temperature ferromagnetic state remains typical of a doped semiconductor, supporting the view that this material is semiconducting in its ground state and that no metal-insulator transition occurs at the Curie temperature.

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I. INTRODUCTION

The rare earths (RE) have found application in a number of important technologies, most notably in electronic and optoelectronic devices and in strong permanent magnets. Within these fields there are reports of surprisingly advantageous marriages with nitrogen. Thus, in RE magnets it is known that the incorporation of nitrogen interstitials renders the material magnetically harder,[1] and there are reports of enormously enhanced moments associated with substitutional Gd in GaN.[2] It is clearly important to understand the physics of RE ions in their bonding configurations with nitrogen. Given this importance it is interesting that the end member of any of these materials, the RE mononitrides, is a remarkably poorly understood class of materials.

The rare-earth nitrides have been characterized as regards their magnetic behavior, but the most fundamental question about their conductivity, whether they are semiconducting or metallic in their ground state, has remained unanswered for some years. The most thoroughly studied of these is GdN, and although early studies produced conflicting results regarding the magnetic ordering,[3,4] GdN is now generally accepted to be ferromagnetic below about 70 K with a saturation moment of $\sim 7\mu_B/\mathrm{Gd}$.[5–11] More recently, advanced band structure calculations that take into account the magnetic order have predicted a range of electronic structures in the ferromagnetic ground state of GdN. Aerts *et al.*,[12] using density functional theory in the local-spin-density approximation with a self-interaction correction, found that exchange splitting of the predominantly Gd *s*-*d*-like and N *p*-like conduction band states is sufficient to cause GdN to be half-metallic, meaning that there are mobile electrons at the Fermi level of one spin only. Such materials are of particular interest in the developing field of spintronics. That prediction contrasts sharply with the work of Hasegawa *et al.*,[13] who found a band gap of about 0.3 eV. Similarly, Lambrecht[14] used a novel technique for estimating the quasiparticle correction to the local-density approximation to predict a gap of about 0.7–0.85 eV in the ground state of GdN, which is then a ferromagnetic semiconductor. Semimetallic behavior has also been predicted,[15] with a transition to a half-metal and ultimately an insulator with tensile strain.[16]

Experimental testing of these predictions is challenging due to the difficulty in preparing fully stoichiometric GdN without large concentrations of N vacancies, and due to the rare-earth nitrides' strong propensity to oxidize in the presence of water vapor in the atmosphere. Both nitrogen vacancies and substitutional oxygen act as dopants to provide charge carriers; furthermore, each of these impurities alters the lattice constant and magnetic behavior so that GdN has variously been observed to be metallic above 80 K,[17,18] or insulating,[19] and optical transmission measurements have found that there is an optical gap of ~2 to 4 eV.[20,21] Recent measurements[22] on thin films show a peak in the resistivity that coincides with the Curie temperature, interpreted in terms of a metal-insulator transition induced by exchange splitting of the conduction band. The authors note the similarity of the behavior to that of EuO.[23] However, unlike EuO, the exchange mechanism that gives rise to the magnetic behavior in GdN is not yet clear,[3,5,7,8,24,25] and the role of charge carriers in mediating the exchange is not understood.

In this paper we address the electronic properties of GdN by reporting optical, transport, and magnetic measurements on films of GdN grown by evaporating Gd metal in the presence of N_2 gas. This very simple growth procedure is demonstrated to result in nanocrystalline GdN films with low carrier concentration. We have extensively investigated the temperature-dependent resistivity of the films below room temperature, supported by a determination of the effect of N vacancies.

II. EXPERIMENTAL DETAILS

The films used in this study were prepared in an UHV chamber that had been pumped to 4×10^{-8} mbar and filled during growth with high-purity flowing nitrogen gas to 10^{-4} mbar. GdN was deposited onto substrates at ambient temperature by thermal evaporation of Gd in the presence of this nitrogen gas background. The GdN growth rate was maintained at a constant 1 Å s^{-1}, controlled by the Gd evaporation rate and monitored throughout by a piezoelectric quartz crystal monitor positioned at the center of the substrate holder. Oxygen is known to significantly alter the magnetic and structural characteristics of bulk GdN,[3,7,8] so to

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limit its incorporation the N_2 gas was passed through an Aeronex Ni sponge scrubber and the partial pressures of residual gases in the UHV chamber were recorded with a residual gas analyzer. The partial pressures of O_2 and H_2O were maintained at less than 3×10^{-7} mbar during film growth. These values fell with time during film growth, coinciding with evaporation of the Gd, demonstrating the effectiveness of gadolinium as a getter for these contaminant gasses. As even the bulk rare-earth nitrides are sensitive to moisture,[18,26] the films used for *ex situ* studies were passivated by a layer of either MgF_2 or GaN grown before exposing the films to the venting nitrogen gas and atmosphere. These capping layers were grown to a thickness of typically 50–150 nm by either thermal evaporation (MgF_2) or by ion assisted deposition (GaN). We have extensively reported the properties of GaN films grown in this way in earlier publications.[27–30] Neither capping material affects measurements of the relatively high conductivity of the GdN films. The success of the capping procedure is demonstrated by the fact that secondary ion mass spectra (SIMS) show only Gd and N, and no evidence of oxygen in the GdN layers within the detection limit.

The resistance was monitored during film growth across a gap between predeposited Ag contacts on a sapphire substrate. The conductance was observed to increase linearly with the deposited thickness, confirming that the films are uniform and that the measurements probe the bulk of the film. Postdeposition *in situ* temperature-dependent measurements were made from 100 to 310 K by cooling and heating of the substrate stage. As described below these were extended to 14 K *ex situ*. The current-voltage characteristics of the films were found to be linear, implying that grain boundary tunneling is not a significant effect, presumably due to the relatively high conductivity of the films and the well-connected nature of the grains.

The extreme reactivity of *uncapped* films is demonstrated during venting of the chamber, even with predominantly N_2, to 1 atm. The residual water vapor in the admitted gas leads to a rapid degradation of the films, with the resistivity climbing to above the $10^8\ \Omega\,\mathrm{cm}$ measurement limit within seconds, and the mass of the exposed films increasing by 25% over a period of hours. In contrast the resistivity of the capped films is unchanged for hours after exposure to air. All *ex situ* characterization and physical property measurements were performed on these capped films.

III. RESULTS AND ANALYSIS

Figure 1 is an x-ray diffraction (XRD) scan of a GdN film capped with MgF_2, taken at 0.5° incident x-ray angle in order to increase scattering from the thin film. The peaks indicated are attributed to cubic structure GdN, and this structure has been confirmed in a transmission electron microscopy study.[31] The [200] peak at $2\Theta\approx41°$ is weaker than expected, suggesting that the films are textured. The lattice constant of the films is 5.01 Å, slightly larger than the reference value for bulk GdN of 4.989 Å. Based on the observation[6] that oxygen significantly reduces the lattice constant of GdN, the expanded lattice in our films supports the SIMS conclusion

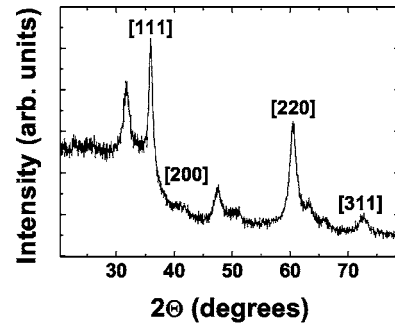

FIG. 1. XRD of GdN capped with MgF_2 taken at grazing incidence. Unlabeled peaks derive from the MgF_2 capping layer.

that O is not a serious contaminant. The films are clearly nanocrystalline as signaled by the width of the XRD peaks; fitting the most prominent with the Debye-Scherrer formula yields an average crystallite size of about 10 nm. The nanocrystalline nature is confirmed by TEM results.[31] There are no secondary phases detected in the XRD spectra and no discernible differences in the XRD scattering from GdN films capped with MgF_2 or GaN.

The magnetic character of the films was measured with a Quantum Design MPMS superconducting quantum interference device. The data of Fig. 2 show the temperature-dependent magnetization of a GdN film capped with GaN measured in an applied field of 50 mT. The magnetization increases rapidly below 70 K and saturates near 5 K. Above 100 K the magnetic response obeys the Curie-Weiss form with a transition temperature of 68 K. Magnetic hysteresis and saturation are observed in the film at 5 K (inset of Fig. 2) with a remanence of $2.74\mu_B/\mathrm{Gd}$ and a coercive field of around 220 Oe. The saturation moment per Gd in a field of 6 T is $6.4\pm0.6\mu_B$. The magnetic behavior of our films thus conforms fully to previous measurements on O-free GdN,[9,10,17] and shows no sign of the reduced T_C and increased coercive field seen in earlier studies of O-bearing material.[4,8]

We have demonstrated that N vacancies are the dominant dopants by following the conductivity as the nitrogen concentration is deliberately reduced during one film growth. In this experiment we observed that the in-plane conductivity

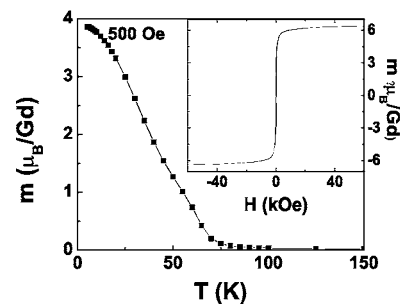

FIG. 2. Magnetic response of a 200 nm thick GdN film capped with GaN. The main window shows the magnetic moment per Gd ion in a field of 0.05 T and the inset is a trace of the magnetization vs applied field at a temperature of 5 K. The coercive field of around 220 Oe is too small for the hysteresis to be visible on this scale.

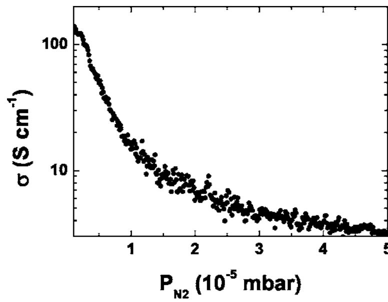

FIG. 3. The conductance of GdN as a function of the pressure of N_2 during deposition, recorded during a growth under a continuously diminishing pressure.

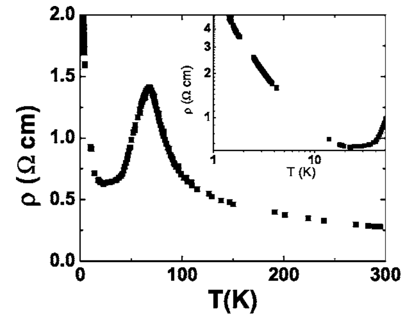

FIG. 4. Temperature-dependent resistivity of a 200 nm thick GdN film. The pronounced peak at 68 K corresponds to the measured Curie temperature of the film. The inset shows the low-temperature behavior of the resistivity.

rises if the nitrogen pressure falls, and its dependence on the pressure head can be determined by noting that, in this geometry, the conductivity is expected to depend on depth. For conductance parallel to the film's surface the depth-dependent conductivity $\sigma(z)$ leads to a measured conductance given by

$$1/R = (W/L) \int \sigma(z) dz, \tag{1}$$

$$\sigma(z) = (L/W) \frac{d(1/R)}{dz}. \tag{2}$$

Here, R is the resistance measured over a path of length L and width W. In Fig. 3 we show the differential conductance [Eq. (2)] recorded while a film is deposited at 2.0 Å s^{-1} as the N_2 pressure in the growth chamber was reduced. In the early stages of growth, when the N_2 partial pressure is at 10^{-4} mbar, the conductance increases linearly with thickness, yielding a resistivity of about 0.3 Ω cm. The conductivity of the growing film begins to increase when the N_2 partial pressure falls below 5×10^{-5} mbar, implying that the films are gaining carriers. As the N_2 pressure is reduced below 2.5×10^{-6} mbar there is a dramatic increase in the conductance corresponding to a change in the film growth to a metallic layer of resistivity smaller than 10^{-2} Ω cm. The implication is that the dominant doping defects are nitrogen vacancies, as has been suggested previously,[4] and the effect of reduced nitrogen content on the conductivity of the films reconciles the previously reported low resistivities of GdN (Refs. 17 and 18) with the insulating nature of GdN films capped with NbN.[19]

We now return to an analysis of uniform films grown in 10^{-4} mbar nitrogen. Figure 4 shows the temperature-dependent resistivity of a GdN film measured *in-* and *ex situ*, after an insulating ($\rho > 10^8$ Ω cm) GaN capping layer was deposited on the top. Note that the ambient-temperature resistivity of 0.3 Ω cm is characteristic of a heavily doped semiconductor, and higher than previously reported values.[18,22] An attempt to fit an activated conduction model to the temperature-dependent behavior above 80 K yields an activation energy of only a few milli-electron-volts, again as would be expected in the presence of heavy doping.

It is important to consider whether the polycrystalline nature of the films might be responsible for the magnitude and temperature dependence of the conductivity. There are many examples of both inhomogeneous composites and even homogeneous metals in which a negative temperature coefficient of resistance is observed, and ultimately it is only the zero-temperature limit of the conductivity that uniquely signals the absence of extended states at the Fermi level characteristic of a semiconductor. However, in the present case the magnitude of the conductivity is inconsistent with a homogeneous metallic nature, for it is several orders of magnitude smaller than can be reconciled with even extreme values of the minimum metallic conductivity, so that we can seek an alternative to the semiconducting nature only within an inhomogeneous model. Thus, the question might be raised that GdN is metallic after all, but that there are barriers, most likely oxide barriers, between the 10 nm crystal grains. These films show no evidence at all of secondary phases in their XRD patterns, they are stoichiometric to within the few percent measurement accuracy achieved, and there is no evidence of impurity ions, especially oxygen, at levels as high as 1%. There are no secondary phases present at concentrations larger than 1%, so it is highly improbable that the observed conductivity is dominated by the grain boundaries.

To provide further evidence we have supplemented the dc measurements by seeking evidence of a band gap by optical reflection-transmission measurements, displayed in Fig. 5. Looking first at the transmission the film is opaque above 2.5 eV, but there is a rapid increase in the transmission at lower energies, indicating the presence of an optical gap near 1.5 eV. There is no evidence at all for a Drude response that would indicate a metallic component. The reflectivity shows little frequency dependence other than the interference pattern from the GaN capping layer. Thus, the ambient-temperature optical response of the films is in excellent agreement with a semiconducting model.

Turning again to the resistivity, it can be seen to indicate a transition to a more conductive state in the low-temperature ferromagnetic phase, falling from a maximum at 68 K, the magnetic ordering temperature. The decrease in resistivity below this temperature is by a factor of 2.3, somewhat large to be associated with only an expected reduction in spin-dependent scattering of charge carriers brought on by the long-range magnetic ordering of spin moments in the film,

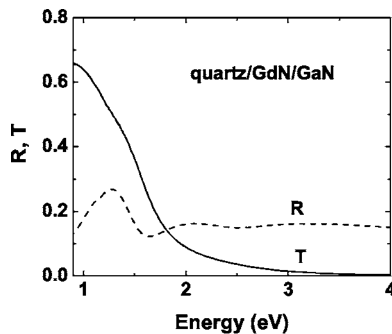

FIG. 5. Optical reflection and transmission for GdN capped with GaN. The strong absorption onset between 1.5 and 2 eV supports the semiconducting model for the film's room-temperature conductivity.

but the low-temperature conductivity is still too small to indicate a transition to a metallic phase. That such a large change can be induced in the resistivity by the onset of ferromagnetism, a bulk effect, further supports the conclusion that the observed conductivity is not dominated by grain boundaries but is representative of the bulk material.

At 22 K the resistivity reaches a minimum and begins to increase as the temperature is further lowered, reaching a value of 5 Ω cm at 1.4 K, about 18 times the room-temperature value (Fig. 4 inset). This indicates that the films are still semiconducting at $T < T_C$. The inference we draw is that the bands shift as the temperature is lowered and the film enters the ferromagnetic phase, leading to the predicted[15] reduction of the gap in the ferromagnetic state, but that the ferromagnetic state is still semiconducting. The Fermi level now lies closer to, but not above, the majority spin conduction band minimum. Thus, the present results confirm the existence of a band gap in stoichiometric GdN in the low-temperature phase, in contrast to theoretical predictions of half-metallic[12] or semimetallic[15] behavior. It is significant that Leuenberger *et al.* observed a similar, though rather weaker resistivity peak than ours in their GdN films.[22] Their films were both more conductive and displayed a weaker temperature dependence than ours, and the authors acknowledge donor impurities such as N vacancies are a likely cause for the high conductivity.

Finally, we comment on the observed ferromagnetic transition temperature, and its implications for the ferromagnetic exchange mechanism.[16] The Curie temperature of our films, measured either by extrapolating the paramagnetic region of the magnetization curve or from the peak in the resistivity, is at the upper limit of values reported in the literature.[6,7,17,21] On the other hand, we have shown above that the carrier concentration is amongst the lowest reported. This implies that the ferromagnetic exchange is intrinsic in nature, rather than being due to a carrier mediated mechanism such as Ruderman-Kittel-Kasuya-Yosida (RKKY).

IV. CONCLUSIONS

In summary, we have determined that GdN thin films can be grown by evaporation of Gd in an environment of 10^{-4} mbar of nitrogen gas, and that they show semiconducting behavior in both the paramagnetic and ferromagnetic states above and below a Curie temperature of 68 K. The conductivity is strongly dependent on the pressure of nitrogen during growth, implying that N vacancies are the dominant dopant, and providing a framework in which to understand previous contradictory results concerning the conductivity of GdN. There is a substantial increase in conductivity upon entering the ferromagnetic state which suggests a reduction of the band gap across the para- to ferromagnetic transition, but the films remain semiconducting in the low-temperature ferromagnetic phase.

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