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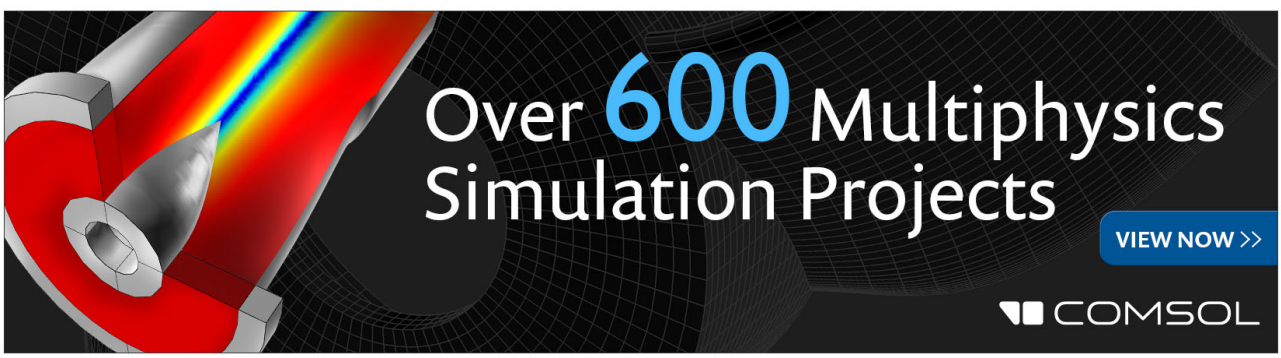

Enhanced Curie temperature in N-deficient GdN

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Polycrystalline GdN thin films have been grown at room temperature with varying N_2 pressure. By varying the nitrogen pressure during growth we alter the carrier concentrations of the films. Films grown at low nitrogen pressures display onset of magnetization at temperatures as high as 200 K and a resistivity of 0.3 mΩ cm, whereas films grown at high nitrogen pressures all show a Curie temperature very close to 70 K and resistivity ranges over 1–1000 Ω cm are observed. For all GdN films a peak in the resistivity occurs at T_C. © *2011 American Institute of Physics*.
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The rare-earth nitrides have a clear role to play in the exploration of spintronics structures.[1–4] They condense into the NaCl structure, forming a series of epitaxy-compatible materials with contrasting magnetic properties. Most are ferromagnetic at low temperature, and both semiconductors and half metals are predicted by theoretical treatments.[2–9] GdN has the highest Curie temperature, 65–70 K, and a 7 μ_B moment per cation[10–14] similar to EuO.[15–20] GdN is a narrow-gap semiconductor[21] with n-type carriers from N-vacancy (V_N) donors,[12,14] while EuO is an insulator with a 1.12 eV band gap.[15] T_C can be enhanced in EuO by electron doping with oxygen vacancies or with Gd or La substitution,[16–18] although the physics of this enhancement is debated.[15,16,18,20] Here we demonstrate a similar enhancement in N-deficient GdN, raising the prospect of utilizing such films in spintronics devices operating above liquid nitrogen temperature.

The theoretical description of ferromagnetic order in GdN is still unclear. A local spin density approximation (LSDA)+U treatment predicts a Curie temperature of only 10 K for GdN,[8] prompting a suggestion that carrier-mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange enhances T_C to 70 K.[4] A resistivity anomaly similar to that in EuO occurs at T_C, although its detailed nature has not been investigated.[10,11] This paper reports the magnetic response and electrical conductivity of polycrystalline GdN films with varying V_N concentration. The Curie temperature settles at 70 K for all films with modest or low ($<10^{21}$ cm^{-3}) carrier concentration, the concentration range across which RKKY is predicted to become active.[4] The most N-deficient films, with V_N and carrier concentrations approaching 10^{22} cm^{-3}, exhibit a significantly enhanced T_C.

Thin films of GdN were grown in a chamber pumped to a base pressure of 5×10^{-9} Torr. Sapphire and silicon substrates were indium bonded onto a 2 in. Si carrier wafer and out-gassed at 130 °C for 1 h before being allowed to cool to room temperature for 2 h. Gd metal was evaporated by using an electron beam at a rate of 0.1 nm/s in 5×10^{-7} to 2.6 $\times10^{-4}$ Torr of nitrogen. The reflection high energy electron diffraction (RHEED) pattern of such films results in well-resolved Debye rings characteristic of a polycrystalline layer. The samples were capped *in situ* with a 35 nm AlN film deposited at a rate of 0.01 nm/s in the presence of activated nitrogen. The GdN films were then characterized by x-ray diffraction (XRD), and Rutherford backscattering spectrometry confirmed thicknesses near 200 nm. The in-plane magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. Electrical transport measurements were carried out using a Van der Pauw configuration and pressed indium contacts with contact resistances less than the sheet resistance of the films.[10]

The XRD diffractograms of the GdN samples grown on c-plane sapphire substrates are shown in Fig. 1, with the expected position of Gd and GdN peaks labeled, along with the sapphire peak at 41.8° [0006]. Note that the Gd ion density in GdN is almost identical to that in metallic Gd, so that the Gd [002] and GdN [111] reflections overlap. For the sample grown at 5×10^{-7} Torr the XRD shows predominantly Gd metal, with [100], [101], and [002] orientations all present, though a small GdN [111] feature might be obscured by the overlapping Gd [002] line. By contrast, there are clear signatures of GdN in all samples grown with N_2 pressures of

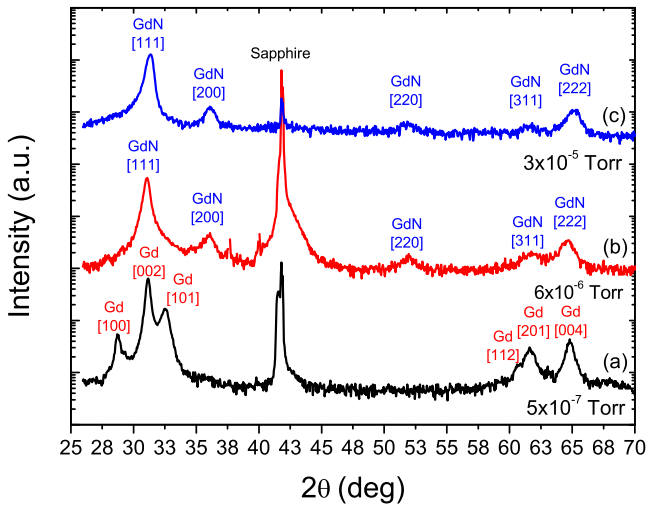

FIG. 1. (Color online) XRD difractograms for GdN films grown under nitrogen pressures of (a) 5×10^{-7} Torr, (b) 6×10^{-6} Torr, and (c) 3×10^{-5} Torr.

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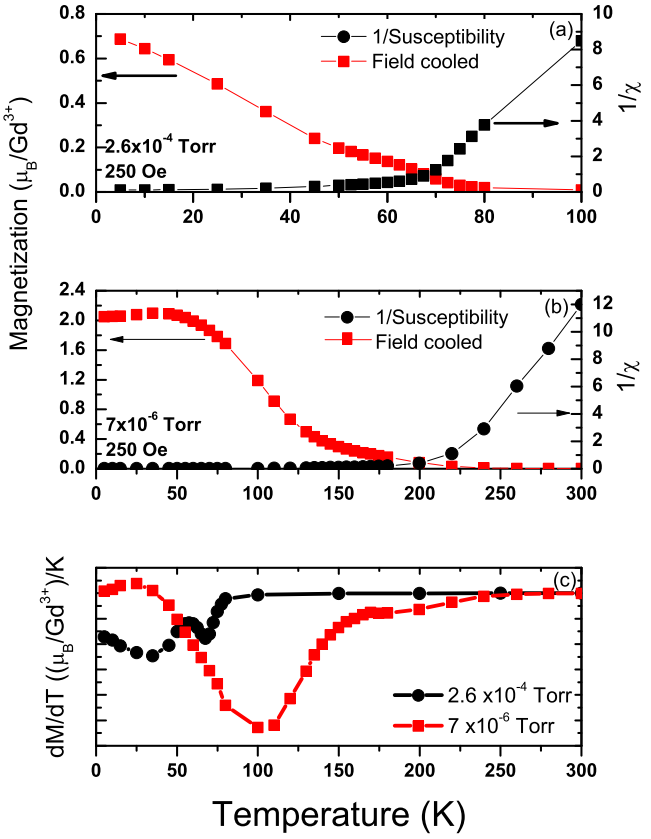

FIG. 2. (Color online) Field cooled magnetization and inverse susceptibility. The nitrogen growth pressure is (a) 2.6×10^{-4} Torr and (b) 7×10^{-6} Torr and the applied field is 250 Oe. Plot (c) shows the derivative of the field cooled data from (a) and (b).

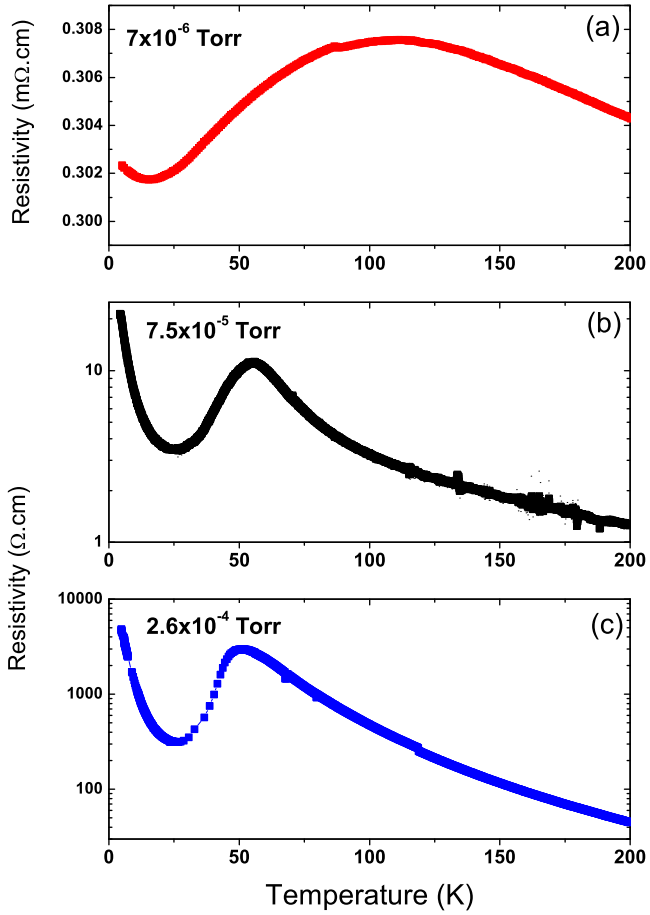

FIG. 3. (Color online) Temperature dependent resistivity for samples prepared under nitrogen pressures of (a) 7×10^{-6} Torr, (b) 7.5×10^{-5} Torr, and (c) 2.6×10^{-4} Torr.

6×10^{-6} Torr and above [Figs. 1(b) and 1(c)]. In particular, GdN [200] and [220] reflections are seen at 35.9° and 51.6°, respectively, which have no closely spaced Gd peaks to cause ambiguity. Most significantly, for growth pressures of 6×10^{-6} Torr and above there is no Gd at the detection limit of ~5%, and the ratio of GdN [111] to GdN [200] peak intensities is the same in all such samples. Thus all films grown above 6×10^{-6} Torr are single phase GdN with V_N concentrations of up to a few percent.[22] The crystallite sizes are about 10 nm.

Figure 2 shows the field-cooled and zero-field-cooled magnetic moments of films deposited on Si (100). The sample grown at the highest pressure, 2.6×10^{-4} Torr [Fig. 2(a)], shows a Curie–Weiss response with paramagnetic T_C of 70 K and a rapidly rising response below that temperature, as do all films grown at pressures above 3×10^{-5} Torr. The film grown at 5×10^{-7} Torr [Fig. 1(a)] shows the 293 K T_C of metallic Gd. The common T_C in films grown at modest N_2 pressure (low V_N density) establishes an intrinsic 70 K T_C. One might still ask whether there is an additional RKKY exchange, and indeed we find an enhanced Curie temperature for the most nitrogen-deficient films in our study. Thus in Fig. 2(b), for a sample grown at 7×10^{-6} Torr, there is an onset of ferromagnetic behavior at 200 K.

It is important to note that this enhanced ordering temperature is signaled not only by a steep rise in magnetization but also by the Curie–Weiss dependence in the paramagnetic state. The inverse susceptibility is linear in temperature above the magnetic transition, where a slope that is related to the paramagnetic moment (μ=7 μ_B) of N Gd^{3+} ions per unit volume participating in the ferromagnetic phase is $(k_B/N\mu^2)$. Here k_B is the Boltzmann constant. The slope of the inverse susceptibility in Fig. 2(b) then establishes that 75% of the Gd ions in the film participate in the exchange that precipitates the ferromagnetic transition at 200 K. This is further supported by the very large ferromagnetic moment of 1 μ_B/Gd in conditions (250 Oe, 100 K) far from saturation and well above the 70 K Curie temperature of stoichiometric GdN. Clearly the majority of Gd ions contribute to the 200 K ferromagnetic transition; it cannot be related to a secondary phase so dilute as to be missed in XRD.

To investigate the samples further the derivative of the magnetization with respect to temperature is plotted in Fig. 2(c) for both the stoichiometric GdN sample and the nitrogen-deficient film. The film grown at 2.6×10^{-4} Torr shows structure at 70 K and a second structure at 35 K which we believe signals the blocking temperature of superparamagnetism arising from the nanocrystalline structure of the films. The nitrogen deficient sample in contrast has no structure at 70 K, rather there is a strong peak at 100 K and a smaller feature centered on 200 K. Such a rise in T_C and additional structures in the magnetization derivative plots have also been observed in Gd doped EuO films, where some treatments attribute the enhanced T_C to bound magnetic polarons centered on Gd ions that then polarize the surrounding EuO.[16] It can be speculated that the 6-ion Gd cluster surrounding a V_N plays a similar role.

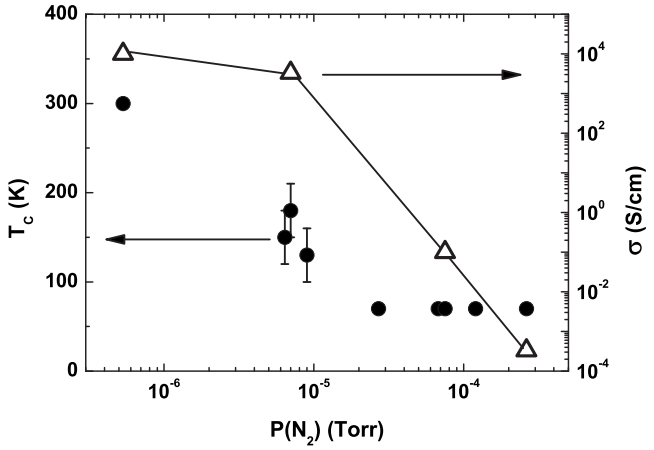

FIG. 4. Curie temperature (T_c) and conductivity (σ) just above T_c, as a function of sample growth pressure. The points around 125–200 K have error bars determined by the less than 100% contribution of Gd ions in the paramagnetic phase.

We turn next to the temperature-dependent resistivity (Fig. 3). The magnitude of the resistivity increases as the V_N concentration falls with increased nitrogen growth pressure, as observed previously.[10,14] The films all show an anomaly at T_C. Taking the conductivity just above T_C as a measure of the carrier concentration it can be seen that this parameter varies by seven orders of magnitude between the most and least conductive films. The resistivity anomaly follows T_C as it is enhanced from 70 K to above 100 K. Interestingly the highest pressure sample not only shows a resistivity in the range of 10^3 Ω cm, but also the anomaly at T_C is over an order of magnitude, substantially larger than in other reports.[10–14]

We draw these results together by plotting the Curie temperature and conductivity versus the growth N_2 pressure in Fig. 4. It is immediately noticed that T_C lies near 70 K for a four-decade range of conductivity found for growth pressures between 2×10^{-5} and 5×10^{-4} Torr. The carrier densities inferred by their conductivities at T_C are in the range of 10^{15}–10^{21} cm^{-3} as has also been corroborated by Hall measurements.[12,14] An RKKY-enhanced T_C has been predicted for the larger of these carrier densities,[4] but such an enhancement is entirely absent in the data. Evidently 70 K is the intrinsic Curie temperature of near stoichiometric GdN. An enhancement appears only for films with carrier concentrations of around 10^{22} cm^{-3} where the conductivity approaches that expected of metals, larger than 10^3 S/cm.

In summary we have grown a sequence of GdN films at room temperature with constant Gd flux but varying N_2 pressure. For all samples grown at pressures of 6×10^{-6} Torr and above we observe GdN films. Films grown between 6×10^{-6} and 1×10^{-5} Torr have an onset of ferromagnetism at 125–200 K. Films grown under N_2 pressures above 3×10^{-5} Torr all show T_C very close to 70 K. The resistance of the films all show an anomaly at T_C and a magnitude increasing with the N_2 growth pressure. The role of nitrogen defects in the behavior of GdN thin films is more complex than only adding charge carriers and by controlling the nitrogen content of the GdN films during growth we can raise the T_C of the material maintaining electronic and magnetic correlation.

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