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Large negative magnetoresistance in reactive sputtered polycrystalline GdN$_x$ films

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Polycrystalline ferromagnetic GdN$_x$ films were fabricated at different N$_2$ flow rates ($f_{N_2}$) to modify N-vacancy concentration so as to study its influence on electric transport. Metal-semiconductor transition appears at Curie temperature ($T_C$) of ~40 K. Temperature-dependent magnetoresistance (MR) shows a peak at $T_C$. The films at $f_{N_2} = 5, 10, 15,$ and 20 sccm show MR of $-38\%$, $-42\%$, $-46\%$, and $-86\%$ at 5 K and 50 kOe, respectively. Above 15 K, MR is from colossal MR and from both colossal and tunneling MR below 15 K. The enhanced MR at $f_{N_2} = 20$ sccm is attributed to large spin polarization of half-metallicity in GdN$_x$ with low N vacancies. © 2013 AIP Publishing LLC.

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GdN show interesting magnetic, electronic transport, and optical properties due to partially filled 4f orbital that makes it ferromagnetic below Curie temperature ($T_C$) of 65–70 K with a magnetic moment of $7\mu_B$/Gd$^{3+}$, However, the origin of magnetism in GdN is controversial. Recently, Duan et al. suggest that a next-nearest-neighbor antiferromagnetic superexchange interaction coexists along with RKKY nearest-neighbor interaction. Calculations by Mitra et al. reveal that, in addition to 4f moments ($7\mu_B$), a small 5d moment appears on Gd site due to $f-d$ exchange. Furthermore, the electrotransport of GdN has also remained a debatable issue, due to the difficulty of preparing ordered samples with stoichiometric Gd:N ratios and low oxygen levels. Room-temperature resistivity of GdN is in a wide range from $10^{-2}$ to $10^0$ cm for epitaxial films and from 1 to 10 cm for polycrystalline films. The dominant dopants are N vacancies and the carriers with concentrations of $10^{-20}$ cm$^{-3}$ are electrons. GdN is half-metallic, semiconducting, and insulating behaviors are reported in GdN$_x$. A magnetoresistance (MR) peak near $T_C$ can reach 35% and 27% observed by Ludbrook et al. and Leuenberger et al., respectively. However, the spin-dependent electrotransport and its dependence on N-vacancy concentration are still not clear. In our previous studies on the nitride and oxide films, the N or O atomic fraction increases with the increase of N$_2$ or O$_2$ partial pressures. Therefore, N-vacancy concentrations in GdN$_x$ films can be modulated by controlling the N flow rates. Meanwhile, if GdN is half-metallic with high spin polarization, the tunneling MR across grain boundaries may appear in polycrystalline samples.

In this letter, polycrystalline GdN$_x$ films with different N-vacancy concentrations were investigated. The films present a metal-semiconductor transition at $T_C$, and the films are ferromagnetic below $T_C$. A large MR of ~86% is observed in the film fabricated at a N$_2$ flow rate ($f_{N_2}$) of 20 sccm. The origin of large MR is attributed to both colossal MR inside grains and tunneling MR at grain boundaries. The appearance of tunneling MR suggests that GdN$_x$ film at $f_{N_2} = 20$ sccm has a large spin polarization.

GdN$_x$ films were fabricated on MgO(100) wafers by dc reactive facing-target sputtering from a pair of pure Gd targets (4 N) with a base pressure better than $8\times10^{-6}$ Pa. The sputtering pressure was kept at 1.0 Pa with a total 100-sccm gas mixture of Ar (5 N) and N$_2$ (5 N), where $f_{N_2}$ was set at 5, 10, 15, and 20 sccm. The substrate temperature was kept at 550°C during deposition. The film thickness was ~200 nm determined by a Dektak 6M surface profiler. About 100-nm thick AlN layer was deposited on GdN$_x$ films as a protection coating. The crystalline structure was characterized by x-ray diffraction (XRD). The magnetic properties were measured by a Quantum Design superconducting quantum interference device-vibrating sample magnetometer. The electrotransport properties were measured by a Quantum Design physical property measurement system with a standard four-terminal method. All of the measurements were performed on the samples immediately after being taken from the sputtering chamber because the sample could be damaged by exposing in air.

Figure 1(a) shows the typical XRD pattern (0–20) of GdN$_x$ film on MgO(100) substrate. The peaks at 30.4° and 35.2° are from face-cubic-centered (fcc) GdN(111) and (200). The peaks at 28.4° and 32.7° are from MgO substrates as these peaks also appear in XRD pattern of a bare MgO substrate, even though they are labeled as fcc Gd(100) and (101) by Plank et al. and Senapati et al. After that, the sample was rotated by 35.3° and the tilting scan was performed, as labeled in the inset of Fig. 1(a). The diffraction peaks are from fcc GdN$_x$. From above analyses, one can conclude that the films are composed of polycrystalline GdN$_x$, but are not epitaxial. Meanwhile, the broad XRD peaks suggest the presence of disorder in polycrystalline GdN$_x$ films. In our previous studies on polycrystalline CrN$_x$, FeN$_x$, and FeO$_x$, films fabricated using the same methods, the disordered grain boundaries...
with a thickness of about 2-3 nm between the grains with different orientations have been observed,\textsuperscript{20,21,24} which serves as a tunneling barrier at low temperatures. So, the disordered grain boundaries should also exist in the present polycrystalline GdN\textsubscript{x} films. Therefore, the structure of GdN\textsubscript{x} film on MgO(100) wafer can be illustrated as Fig. 1(b).

Figure 1(c) shows the $M$–$T$ curves of GdN\textsubscript{x} films fabricated at different $f_{N2}$. It is clear that the magnetization fast increases with the decreased temperature below 50 K. The temperature-dependent magnetization is consistent with previous reports on GdN,\textsuperscript{19,25} revealing that the magnetization is from GdN\textsubscript{x}. The film fabricated at $f_{N2} = 20$ sccm shows an upturn of magnetization below 20 K, which is similar to the shoulder observed in the intermediate-doped epitaxial GdN film.\textsuperscript{26} The shoulder is ascribed to the formation of magnetic polarons centered on N vacancies.\textsuperscript{26} Similarly, at $f_{N2} = 20$ sccm, the upturn of magnetization below 20 K can be attributed to the ferromagnetism brought about by N vacancies when carriers freeze out of conduction band to occupy $V_N$ level and provide a large local electron density that can mediate exchange between neighboring Gd ions, forming a magnetic polaron. Figure 1(d) shows the temperature-dependent normalized resistivity $\rho(T)/\rho(305\,\text{K})$ of polycrystalline GdN\textsubscript{x} films. In the inset of Fig. 1(d), the dependence of room-temperature resistivity on $f_{N2}$ is given. It is clear that the room-temperature resistivity slowly increases from 0.30 $\Omega$cm at $f_{N2} = 5$ sccm to 0.45 $\Omega$cm at $f_{N2} = 15$ sccm, and then quickly increases to 1.78 $\Omega$cm at $f_{N2} = 20$ sccm. The change of room-temperature resistivity can be ascribed to the decrease of N vacancies that can affect the density of states at Fermi level, as shown in the following paragraphs. The room-temperature resistivity (0.30–1.78 $\Omega$cm) has the characteristic of a doped semiconductor. In high-temperature range, the resistivity increases with the decrease of temperature, showing a semiconducting conductance. However, the metallic conductance mechanism dominates in low-temperature range. Obviously, all of GdN\textsubscript{x} films show a metal-semiconductor transition at $T_C$ of about 40 K. With the increase of $f_{N2}$, the metal-semiconductor transition temperature increases from 36 K at $f_{N2} = 5$ sccm, 41 K at $f_{N2} = 10$ sccm to 44 K at $f_{N2} = 15$ sccm, then decreases to 38 K at $f_{N2} = 20$ sccm, which is related to N vacancies, as reported by Plank et al.\textsuperscript{13} The metal-semiconductor transition becomes obvious and the full width at half height becomes narrow with the increased $f_{N2}$ due to the decrease of N-vacancy concentration. Below $T_C$, the spin moments show long-range ferromagnetic ordering, bringing on a reduction in spin-dependent scattering of charge carriers, i.e., the decrease of resistivity. The resistivity reaches a minimum at 15 K and then increases as temperature further decreases, which can be attributed to the charge carriers tunneling between grains.\textsuperscript{27}

MR–$H$ curves of GdN\textsubscript{x} films are shown in Figs. 2(a)–2(d), where the magnetic field is perpendicular to the film plane. MR is defined as

$$\text{MR} = \left[ \frac{R(H)}{R(0)} - 1 \right] \times 100\%,$$

where $R(H)$ and $R(0)$ refer to the resistance measured with and without the magnetic field, respectively. The shapes of MR–$H$ curves for the films fabricated at $f_{N2} = 5, 10,$ and 15 sccm are identical, where MR is $-38\%$, $-42\%$, and $-46\%$ at 5 K and 5 kOe, respectively. Negative MR is observed in GdN\textsubscript{x} films at low temperatures and MR increases monotonously with the increased magnetic field. In Fig. 2(e), MR shows a peak, which is similar with colossal MR in perovskite manganites.\textsuperscript{28–30} Therefore, we adopt the model developed for MR–$H$ curves in perovskite manganites,\textsuperscript{28–30} where MR follows Brillouin function $B_j$,

$$\text{MR} \approx -\beta_j \left( \frac{\mu_{\text{eff}}H_j/k_BT}{1} \right),$$

where $\mu_{\text{eff}}$ is the average local moment and $J = 7/2$. MR–$H$ curves above 15 K can be well fitted using Eq. (2), as the solid line in Figs. 2(a)–2(e). The above characteristics suggest that MR in polycrystalline GdN\textsubscript{x} films is similar with that in perovskite manganites. Below 15 K, MR–$H$ curves cannot be well fitted by Eq. (2) due to the appearance of tunneling conductance at low temperatures that has been detected in temperature-dependent resistivity curve, even though the spin polarization of the films with different N vacancies may be different. In Fig. 2(e), one can find...
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Distinguished characteristics for the film fabricated at $f_{N2} = 20 \text{ sccm}$ compared to the samples fabricated at $f_{N2} = 5$, 10, and 15 sccm: (1) At $f_{N2} = 20 \text{ sccm}$, MR reaches $\sim 86\%$ at $5 \text{ K}$, which is almost twice larger than that of the films fabricated at lower $f_{N2}$; (2) Low-temperature MR changes significantly with temperature; (3) The largest MR appears at $5 \text{ K}$ even though there is a peak at $T_C$ in MR-$T$ curve. These distinct MR characteristics suggest that different mechanisms contribute to MR at $f_{N2} = 20 \text{ sccm}$, which will be discussed in the following paragraphs.

The $M-H$ curves of GdN$_x$ films at $5 \text{ K}$ are plotted in Fig. 3(a), showing that GdN$_x$ films are ferromagnetic. The saturation magnetization ($M_s$) of GdN$_x$ films at $f_{N2} = 5$, 10, 15 and 20 sccm is 727, 745, 1063, and 920 emu/cm$^3$, respectively. Meanwhile, the shape of $M-H$ curves is similar. Therefore, at $f_{N2} = 20 \text{ sccm}$, the largest MR should not be related to the magnetization. Figure 3(b) shows the temperature-dependent $M-H$ curves of GdN$_x$ film fabricated at $f_{N2} = 15 \text{ sccm}$. Ferromagnetic ordering becomes weak with the increased temperature and the hysteresis characteristic disappears above $50 \text{ K}$. $M_s$ decreases from 1063 emu/cm$^3$ at $5 \text{ K}$, 705 emu/cm$^3$ at $20 \text{ K}$, to 297 emu/cm$^3$ at $50 \text{ K}$.

In $\rho(T)/\rho(305 \text{ K})$ curves, the resistivity increases as temperature decreases below $15 \text{ K}$, which is ascribed to the charge carriers intergrain tunneling. The question is why only the film fabricated at $f_{N2} = 20 \text{ sccm}$ shows the significantly enhanced MR at low fields, which should be caused by the different spin polarization in the films with different N vacancies. For clarifying this point, Figures 4(a)–4(d) show the electronic band structure of a GdN $2 \times 2 \times 2$ supercell without and with N vacancies. All of the spin-polarized calculations were performed within projector augmented wave (PAW) method as implemented in the computational code of Vienna $ab$ initio simulation package (VASP), based on the density-functional theory (DFT). Exchange-correlation potential was treated using generalized gradient approximation (GGA) according to Perdew–Burke–Ernzerhof (PBE). The valence-electron configuration for N and Gd was chosen as $2s^22p^3$ and $4f^{7}5s^25p^65d^16s^2$, respectively. The strong correlation effects were introduced by Hubbard augmented density functional theory (GGA+$U$) model, where an effective $U_{eff} = U - J = 6.7 - 0.7 = 6.0 \text{ eV}$ was applied to the on-site Coulomb ($U$) and the exchange interaction ($J$) was applied to the f-orbitals of Gd. To find the theoretical equilibrium static geometries for all the cases, a G-centered $6 \times 6 \times 6 \text{ k mesh}$ together with an energy cutoff of $600 \text{ eV}$ was used in geometry optimization process and static calculations. Density of states was calculated using $6 \times 6 \times 6 \text{ k mesh}$ in Brillouin zone. The convergence criteria for total energy and force were $10^{-5} \text{ eV}$ and $0.01 \text{ eV/Å}$. For the calculations of band structure, a series of high symmetry points were used in the Brillouin zone. All of the atoms were relaxed using conjugated gradient method until Hellmann–Feynmann forces on each atom were reduced to less than $0.01 \text{ eV/Å}$. In the calculation methods, GW focuses on corrections to all subsystems containing spd sub-systems, but the $U$ in local spin density approximation (LDA+$U$) focuses on corrections to a particular subsystem.

![Figure 3](image3.png)

**FIG. 3.** (a) $M-H$ curves of GdN$_x$ films fabricated at different $f_{N2}$ measured at $5 \text{ K}$. (b) $M-H$ curves of GdN$_x$ film fabricated at $f_{N2} = 15 \text{ sccm}$ measured at different temperatures.

![Figure 4](image4.png)

**FIG. 4.** Calculated electronic band structure of (a) Gd$_2$N$_{20}$, (b) Gd$_3$N$_{18}$, (c) Gd$_3$N$_{38}$, and (d) Gd$_3$N$_{38}$. The blue lines indicate majority spin states and red lines indicate minority spin states. (e) Schematic illustration of magnetization configuration of GdN$_x$ grains without and with a magnetic field.
For GdN, GW method can describe the occupied 4f states and spd subsystems correctly, but overestimates the unoccupied 4f states and band gaps slightly. The LDA+U method that does not correct d subsystem can reproduce GW (f1, f1) results. In addition, Duan et al. used local spin-density approximation (LSDA+U) to predict the metal-insulator transition in GdN system and the magnetic order change from ferromagnetic in GdN to antiferromagnetic in other Gd pnictides. Moreover, the electronic and magnetic properties of GdN is also calculated using LSDA+U method by Larson et al., and ferromagnetism was predicted by applying U on f and d orbitals. Abdelouahed et al. used GGA+U to calculate the magnetic anisotropy energy of bulk GdN, which produced the best possible agreement with the experimental value. In this work, we only focus on the trend change of band structure of GdN with N vacancies. GGA+U method that does not consider the correlations for d-states is reasonable, and the calculated results of GdN without N vacancies are consistent with previous reported results. In Fig. 4(a), the band structure of majority spin states is metallic in stoichiometric GdN, while that of minority spins shows a band gap of 0.6 eV, indicating a half-metallic character with a large spin polarization of 100%. Herewith, the spin polarization is defined as $P = (N^+ - N^-)/ (N^+ + N^-)$, where $N^+$ ($N^-$) is the density of electronic states at the Fermi level. After N vacancies are introduced, the whole band regions shift towards low energy. When one N atom is lost (Fig. 4(b)), the initial energy bands shift towards lower energy and several impurity energy bands appear, but Gd$_{32}$N$_{31}$ remains spin-polarized with a smaller spin polarization of $P = 56\%$. However, when one more N atom is lost, the band structure becomes metallic. As indicated in Figs. 4(c) and 4(d), Gd$_{32}$N$_{30}$ and Gd$_{32}$N$_{28}$ are metallic either in majority or in minority spin states with a spin polarization of 35% and 40%, respectively. It can be concluded that the large spin polarization only appears at low N vacancies. Meanwhile, in tunneling MR polycrystalline systems, MR depends on the spin polarization, where large MR appears as the spin polarization of ferromagnetic grains is large. Therefore, MR at $f_{N2} = 20$ sccm is the contributions from both the colossal MR inside grains and tunneling MR between grain boundaries. Compared with the films at 5, 10, and 15 sccm, the enhanced MR at $f_{N2} = 20$ sccm is from the spin-dependent tunneling between the grain boundaries due to the appearance of large spin polarization. This phenomena is similar with that observed in granular perovskite manganites, as shown in Figs. 4(e) and 4(f). Although the tunneling MR also exists in the films at 5, 10, and 15 sccm, the small spin polarization due to high N vacancies make it a small contribution to total MR.

In summary, polycrystalline GaN$_x$ films are ferromagnetic with $T_C \approx 40$ K. At $T_C$, a metal-semiconductor transition appears. The films fabricated at low $f_{N2}$ shows a MR of about $-40\%$, which is mainly from colossal MR. At $f_{N2} = 20$ sccm, the film presents a very large MR of $-86\%$. The large MR is from the contribution of the colossal MR inside grains and tunneling MR between grain boundaries. This work was supported by NSFC of China (51171126) and Key Project of TSTC of Tianjin (12JCZDJC27100).