Magnetic phases and anisotropy in Gd-doped GaN

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In this work we present a detailed study of the magnetic properties of GaN:Gd layers with different Gd content (6×10^{15} to 1×10^{19} cm^{-3}) grown by reactive molecular beam epitaxy. The temperature dependence of the magnetic properties suggests the existence of at least two ferromagnetic phases with different order temperatures. The coexistence of two ferromagnetic phases is explained within the framework of the phenomenological model, introduced previously by Dhar *et al.* [Phys. Rev. Lett. **94**, 037205 (2005)]. The layers are also found to exhibit a magnetic anisotropy, with the hard axis along the growth direction and an easy plane parallel to the surface. Moreover, the saturation magnetization shows a dependence on the orientation of the magnetic field, which may result from the anisotropy in the polarization induced in the GaN matrix by the internal and external magnetic fields.

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I. INTRODUCTION

The search for magnetic semiconductors with a Curie temperature above 300 K is currently one of the major challenges in semiconductor spintronics. We recently reported room temperature ferromagnetism in Gd-doped GaN (with a Gd concentration below 10^{19} cm^{-3}).[1] In addition to a high Curie temperature (up to 800 K), magnetic measurements reveal an unexpectedly high magnetic moment per Gd atom, as large as $4000\mu_B$/Gd for low doping (below 10^{16} cm^{-3}).[2] This colossal magnetic moment has recently also been observed in GaN implanted with Gd.[3] The ferromagnetic behavior observed in this material cannot be explained by the classical theories of ferromagnetism: the distance between magnetic atoms is too large to allow direct, indirect or double exchange coupling and the material is semi-insulating, ruling out the possibility of coupling via electrons through the Ruderman-Kittel-Kasuya-Yosida interaction. In Refs. 1 and 2, we introduced a phenomenological model which explains the observed results in terms of a large polarization of the GaN matrix by the Gd atoms.

In addition to the colossal magnetic moment, GaN:Gd exhibits a magnetic behavior very different from classical ferromagnets. In particular, the layers show low coercivity and remanence in all directions. This magnetic behavior is also found in other magnetic nitrides[4–9] and in diluted magnetic oxides.[10–13] Diluted magnetic oxides also show different values of saturation magnetization along different crystallographic directions, an effect that has not been observed in classical ferromagnets. Therefore, further efforts are needed to understand the mechanisms inducing ferromagnetism in these wide-band-gap ferromagnetic materials.

In this paper, we present a detailed study of the magnetic properties of GaN:Gd layers grown by reactive molecular beam epitaxy. For this study we have grown more GaN:Gd layers to demonstrate the reproducibility of our magnetization results and here the temperature dependence of magnetization of both previously and newly grown samples has been studied. The dependence of magnetization on temperature reveals the presence of two ferromagnetic phases, one with the same transition temperature for all samples (70 K) and another one which remains ferromagnetic at room temperature and above. The layers exhibit a magnetic anisotropy with the hard axis in the growth direction and different values of magnetic moment in different crystallographic directions. These results can be understood within the framework of the phenomenological model proposed previously.

II. EXPERIMENT

Gd-doped GaN layers with a thickness of approximately 500 nm were grown on 6*H*-SiC(0001) substrates using reactive molecular beam epitaxy (RMBE). The concentration of Gd in these samples ranges from 6×10^{15} cm^{-3} to 1×10^{19} cm^{-3} as measured by secondary-ion mass spectrometry. The structural properties of the samples, studied by reflection high-energy electron diffraction (RHEED), high-resolution x-ray diffraction (XRD), and transmission electron microscopy (TEM), are not different from those of pure GaN. Details on the growth and the structural characterization of these samples can be found in Ref. 1.

The magnetic measurements were done in a Quantum Design superconducting quantum interference device (SQUID) magnetometer in the temperature range from 2 to 360 K. The temperature dependence of the magnetization was recorded at a magnetic field of 100 Oe. Prior to the measurement, the sample was cooled from 360 to 2 K either under a saturating magnetic field of 20 kOe [field cooled (FC)] or at zero field [zero field cooled (ZFC)] after demagnetizing the sample at 360 K with an oscillatory magnetic field. Since the magnetization was measured at a very low magnetic field of 100 Oe, the FC curves are expected to qualitatively represent the temperature dependence of the remanence while the ZFC curves should reflect the temperature dependence of the susceptibility. Unless otherwise stated, the magnetic field was applied in plane, along the $[1\bar{1}00]$ direction for these measurements. For the measurement of the anisotropy, the first magnetization curves (FMCs) were recorded after demagnetizing the sample in an alternating magnetic field and scanning the field from zero to 50 kOe. The magnetic field was applied along different crystallographic directions of GaN. All the data pre-

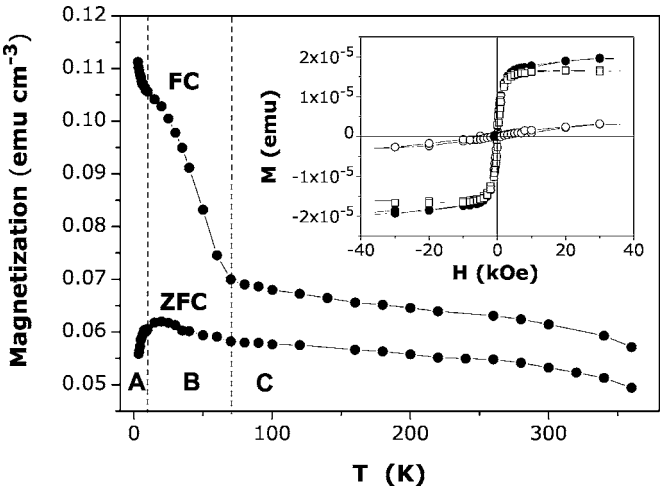

FIG. 1. FC and ZFC curves for a GaN:Gd sample with $N_{Gd}=6\times10^{16}$ cm^{-3} (Refs. 1 and 2). The temperature ranges *A*, *B*, and *C* refer to the three distinct magnetic contributions as discussed in the text. The inset shows the magnetization loops measured at 2 (solid circles) and 10 K (open squares), and the difference between both curves (open circles). It is important to note that the difference was calculated before correcting the diamagnetic background.

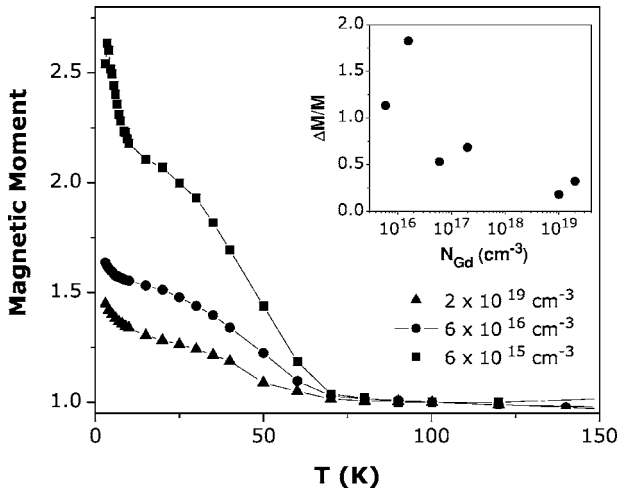

FIG. 2. FC curves for samples with different Gd content. The inset shows an estimation of the change in the magnetic moment at 70 K as a function of the doping.

sented here are corrected for the diamagnetic background of the substrate.

III. RESULTS

A. Magnetic phases

Figure 1 shows the FC and ZFC curves for a GaN:Gd sample with a Gd concentration of 6×10^{16} cm^{-3}. The shape of these curves is very similar for all the studied samples, with a clear increase of magnetic moment in the FC curve below 10 K and a separation between both curves reflecting a hysteretic behavior. For most of the samples, except the highest doped ones, an additional kink at 70 K can be seen in the FC curve, but not in the ZFC curve. Therefore, the temperature dependence of magnetization in this system can be split into three contributions or phases. One contribution (*A*) at low temperature, a second one (*B*) which vanishes at the same temperature (70 K) for all the measured samples, and a third one (*C*) which remains ferromagnetic above room temperature. The Curie temperature of the sample is determined by contribution *C* and depends on the Gd content as reported before.[2]

Magnetization loops measured in the temperature ranges *A* and *B* are clearly different at high field. In the inset of Fig. 1, loops measured at 2 and 10 K are shown. Whereas the latter loop clearly saturates at 0.6 T, the saturation field at 2 K is much higher. In the inset of Fig. 1, the difference between both curves is shown, calculated as $M_{2\ \mathrm{K}}-M_{10\ \mathrm{K}}$ before correcting for the diamagnetic background from the substrate. The shape of this difference suggests contribution *A* to be paramagnetic. The hysteresis loops measured at 50 and 100 K (not shown) are qualitatively similar to the one measured at 10 K, except for smaller values of remanence and coercivity. It is important to remark that we have not found any significant change in saturation magnetization from 10 to 100 K within the resolution of the measurement.

Figure 2 compares the FC curves recorded for samples with different Gd concentrations. The curves are normalized to their values at 100 K. It can be seen that the relative contribution of the transition at 70 K is enhanced when the Gd content in the sample is reduced. The ratio between both components of the magnetic moment can be estimated as

$$\frac{\Delta M}{M}=\frac{(M_{80\ \mathrm{K}}-M_{10\ \mathrm{K}})}{M_{80\ \mathrm{K}}}.$$

In the inset of Fig. 2, this ratio is plotted as a function of the Gd concentration. It is clear that, on the average, this ratio in higher for lower Gd doping in GaN.

The presence of contribution B has also been checked by measuring the temperature dependence of the saturation magnetization M_s and the remanence M_r, calculated from the hysteresis loops measured at different temperatures for a sample with $N_{Gd}=6\times10^{16}$ cm^{-3} (Fig. 3). The temperature dependence of the remanence shows the same two steps at 10 and 70 K as the FC curves. In contrast, the thermal dependence of the saturation magnetization shows one step at about 10 K, whereas the transition at 70 K is absent.

It is worth to mention that the magnetic viscosity effect gives rise to hysteretic behavior in spin glasses and superparamagnetic materials below the transition and the blocking temperature, respectively. However, the isothermal remanent magnetic magnetization in these systems decays on a timescale of minutes to hours. We have carried out isothermal magnetization measurements at 10 and 100 K in different magnetic fields (at remanence, 100 Oe and 10 kOe) after saturating the sample in a field of 50 kOe. No changes in the magnetic moment were observed even after 10 hours within the resolution of our SQUID setup.

B. Magnetic anisotropy

Figure 4 shows the first magnetization curves of a sample with $N_{Gd}=6\times10^{16}$ cm^{-3} for the $[1\bar{1}00]$ (in plane) and [0001]

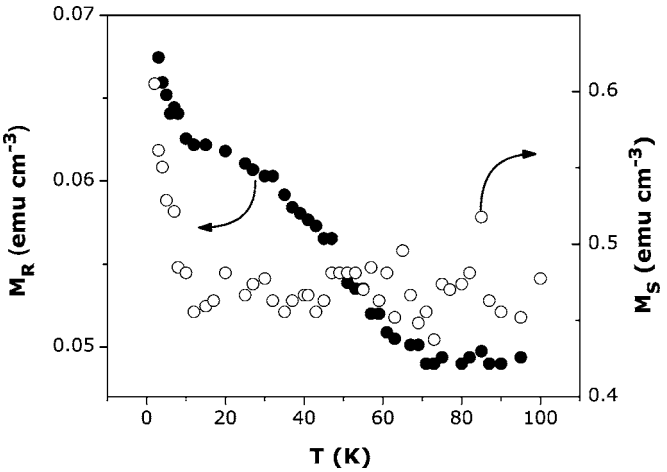

FIG. 3. Temperature dependence of the remanence (solid circles) and the saturation magnetization (open circles) for a GaN:Gd layer with $N_{Gd}=6\times10^{16}$ cm^{-3}.

(out of plane) directions. The first magnetization curve along the perpendicular in-plane direction $[11\bar{2}0]$ is very similar to that obtained along $[1\bar{1}00]$ and it is not shown for sake of clarity. The magnetization has been normalized to the value of the saturation magnetization to allow a better comparison between the different directions. Two different effects related to anisotropy can be observed.

First, there is an easy plane of magnetization perpendicular to the [0001] direction, i.e., [0001] is the hard axis for magnetization. Nevertheless, although it is easier to saturate the sample with a field applied parallel to the surface, it should be noted that also in this case it is necessary to apply a high field ($\simeq10^4$ Oe) to saturate the sample. The energy needed to reach saturation—the so-called anisotropy energy in classical ferromagnets—can be calculated by numerical integration of the first magnetization curve. At 100 K, for example, the value of this energy amounts to $\simeq1500$ erg cm^{-3} for the in-plane compared to $\simeq3000$ erg cm^{-3} for out-of-plane measurements.

The second effect related to anisotropy can be observed in the insets of the figures, where the non-normalized magnetization has been plotted as a function of the applied magnetic field: the saturation magnetization is smaller along the hard axis at all temperatures. This anisotropy in the magnetic moment has been observed in samples with different Gd content and also in samples containing undoped GaN buffer and cap layers.

IV. DISCUSSION

Several magnetic phases have been observed in the temperature dependence of the magnetic moment. The increase in the FC curves at low temperature has also been observed in bare SiC substrates, undoped GaN layers and also in other GaN-based magnetic semiconductors.[4,5,7,14] From the measurements of the hysteresis loops at different temperatures, it seems clear that phase A is not ferromagnetic. Therefore, this phase could be attributed to a change in susceptibility of

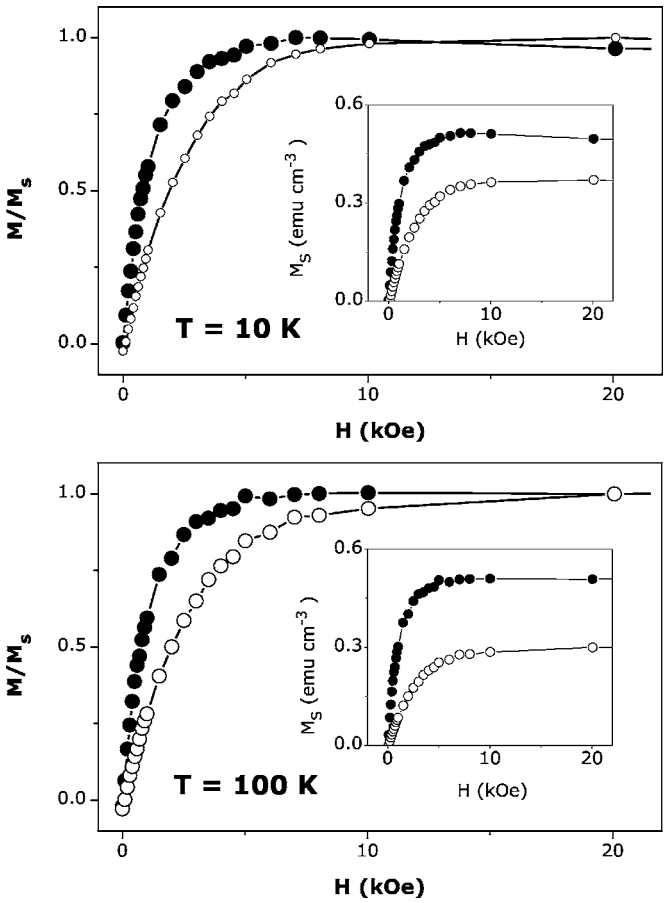

FIG. 4. First magnetization curves measured in two perpendicular directions (open circles [0001], solid circles $[1\bar{1}00]$) for $N_{Gd}=6\times10^{16}$ cm^{-3}. The curves have been normalized to the values of the saturation magnetization. The inset shows the same curves, but not normalized.

GaN or to a small paramagnetic contribution of some dopants in the SiC substrates, not related to the presence of Gd in the layers. However, there is a small increase in the remanence at low temperature and, therefore, the presence of a ferromagnetic phase with Curie temperature around 10 K cannot be completely excluded.

The transition at 70 K has not been observed in undoped samples and is thus related to the presence of Gd in the layer. The Curie temperature for GdN is close to 70 K. However, the structural characterization of these layers by RHEED, XRD, and TEM has not revealed the presence of any cluster or secondary phases in these layers.[1] In order to exclude the possibility of the formation of GdN in the first stages of the growth or after closing the shutters of the effusion cells of the MBE system, we have grown layers with and without buffer and/or capping layers. Furthermore, we have etched a few hundred nanometers from the top of some layers by reactive ion etching. The FC curves of all these layers show the transition at 70 K. Therefore, we believe that this step is stemming from the bulk and not from surface or interface.

In addition to the above considerations, we have not observed any relaxation phenomena in the isothermal behavior of magnetization above and below 70 K. This fact, together

with the absence of any transition in the ZFC curve at 70 K, suggests that contribution *B* is not a superparamagnetic or spin-glass contribution arising from some GdN cluster but a ferromagnetic one.

The colossal magnetic moment of Gd observed in this system has been explained in terms of a Gd-induced spin polarization either of the GaN matrix atoms (Ga and/or N) or of a certain type of defect residing in the matrix.[2] A phenomenological model was proposed associating a sphere of influence with every Gd atom. It was also believed that an overlap of these spheres of influence establishes a long-range magnetic order which could explain the ferromagnetic behavior observed in these samples. In order to achieve such a long-range order it is not necessary that all spheres are interconnected. The situation, in fact, is a well known problem of percolation theory. Within the framework of this theory, a long-range order is expected to occur at the percolation threshold, which is equivalent to the formation of an "infinite cluster" spanning macroscopic regions of the sample. The percolation threshold is reached at a much lower Gd concentration than that necessary to achieve the situation when all spheres are interconnected. In other words, a large fraction of these spheres will still be isolated or form part of small isolated clusters even if the percolation threshold is reached.

It is plausible that the magnetic behavior attributed to phase *B* is in fact resulting from isolated spheres and small isolated clusters while the ferromagnetic behavior with an order temperature above 300 K (phase *C*) is likely to stem from connected spheres, forming clusters comparable in size to the size of the sample. According to this model, the relative magnetic contribution of phase *B* with respect to that of phase *C* should decrease with increasing Gd concentration since the ratio between the volumes occupied by the isolated and connected spheres is expected to decrease as the concentration of Gd is increased. In fact, this trend is seen in the experiments depicted in Fig. 2. The nature of the isolated spheres is expected to be independent of the Gd content of the layer and therefore the same transition temperature for phase *B* is expected in all layers, as indeed observed in the experiments.

We have found a magnetic anisotropy with a hard axis along the direction perpendicular to the surface and an easy plane parallel to the surface in these samples. The presence of magnetic anisotropy in the samples is also a clear indication that the magnetic properties are related to the material itself. The hard axis along the direction perpendicular to the surface cannot be due to the demagnetizing field. Taking into account that the lateral dimensions of the samples are orders of magnitude larger that the thickness, we can assume a demagnetizing factor of 4π along the [0001] direction.[15] The saturation magnetization M_s for the sample investigated here is ≈ 1.8 emu cm^{-3} which results in a demagnetizing field of only 22 Oe at saturation, clearly too small to explain the observed result.

We have observed that the saturation magnetization measured in these samples with an in-plane orientation of the magnetic field is larger than that obtained with the field applied along the out-of-plane direction. The anisotropy in the saturation magnetization, not observed in magnetic nitrides but only recently in some diluted magnetic oxides,[11] leads to a different concept of magnetic anisotropy. These systems are expected to have two contributions to the total magnetic moment: the permanent moment of the magnetic atoms introduced as dopants and the polarization induced in the matrix or in some other dopants or defects by the internal and the external magnetic field.[16,17] When the external field is high enough to saturate the system, the value of the permanent magnetic moment should be constant and independent of the direction of the measurement. However, the polarization of the matrix may be anisotropic, giving rise to the observed effect. Therefore, a new concept of anisotropy arises, related not only to the difference in energy necessary to align permanent magnetic moments along different directions, but also related to the anisotropic polarization of the matrix by the internal and external magnetic field.

V. CONCLUSIONS

Careful studies of the temperature dependence of the magnetic properties of Gd-doped GaN layers provide definite experimental evidence for the existence of three magnetic contributions in the temperature range 2 to 360 K. At low temperature (below 10 K) a nonferromagnetic contribution dominates which is not related to the presence of Gd in the GaN layers. The thermal dependence of the magnetization below 10 K shows paramagnetic behavior. Above 10 K, two ferromagnetic contributions start to dominate, one of them vanishes at 70 K in all studied samples independent of the Gd concentration level ($>10^{15}$ cm^3). The second ferromagnetic contribution persists up to the Curie temperature. The existence of these two ferromagnetic contributions can be nicely correlated with our phenomenological model previously reported in Refs. 1 and 2. The transition at 70 K is more pronounced at low Gd doping of GaN. It is important to note that the observed phenomena are stemming from the bulk of the GaN layers, not from the surface or the interface.

In addition to the dependence of the saturation magnetization M_S on the temperature we have also measured and analyzed the thermal behavior of the remanence M_R in Gd-doped GaN. The results directly support our findings about the three distinct magnetic contributions.

Finally, the Gd-doped GaN layers exhibit a pronounced magnetic anisotropy, with a hard axis along the *c* axis (growth direction) of the wurtzite structure and an easy plane parallel to the surface (*c* plane). In addition to this anisotropy in the magnetization process, we have also observed an anisotropy in the total magnetic moment. A similar behavior has been detected recently in some diluted magnetic oxides, calling for another concept of magnetic anisotropy.

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