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Searching for room temperature ferromagnetism in transition metal implanted ZnO and GaN

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Significant progress in the field of wide-gap dilute magnetic semiconductors (DMS) depends on the discovery of a material system which not only shows high-temperature ferromagnetism but is also simple to prepare and thus easy to reproduce. In this context, ion implantation is an attractive doping method, being both relatively simple and highly reproducible. Here, we report on the search for high-temperature ferromagnetism in ZnO and GaN implanted with Mn, Fe, and Co, prepared under a wide range of implantation and post-processing conditions. We focused on the low concentration regime ($\sim 0.3 - 4\%$) in order to avoid phase segregation and applied strict experimental procedures to avoid ferromagnetic contamination. Despite the wide range of materials, implantation and post-processing conditions, none of the DMS systems showed room-temperature ferromagnetism. These results support the view that dilute transition-metal moments do not order ferromagnetically in ZnO and GaN. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4774102>]

I. INTRODUCTION

The magnetism of wide-gap semiconductors doped with transition metals, or dilute magnetic semiconductors (DMS), remains one of the most puzzling and controversial topics in magnetism today.¹ Despite the more than ten years of intense research and significant developments in both synthesis and characterization methods, none of the wide-gap DMS systems which have been reported to be ferromagnetic at room temperature gathers the consensus of the magnetism community.

The basic condition for the technological relevance of DMS materials is an ordering temperature (Curie temperature T_C) compatible with device operation, i.e., above room temperature. Following the first report of high temperature ferromagnetism in Co-doped TiO₂² and the prediction by Dietl *et al.*³ that highly p-type Mn-doped ZnO and GaN could attain a T_C above room temperature, ferromagnetism at and above room temperature was reported in a rapidly growing number of wide-gap DMS materials (cf., e.g., the reviews Refs. 4–7). Although virtually every attempted impurity-host DMS combination was sooner or later reported to display room temperature ferromagnetism, materials like Co- and Mn-doped ZnO and Mn- and Fe-doped GaN received particular attention.¹ However, as the understanding of the magnetism in these materials deepened, issues of irreproducibility and instability became more evident. As the origin of the observed ferromagnetism became increasingly debated, a number of non-intrinsic sources of ferromagnetism were identified and became well documented: magnetic contamination,^{8–11} measurement artifacts,^{9,10} spinodal decomposition

(e.g., in Co-doped ZnO¹² and Mn-doped GaN¹³) and secondary phase formation (e.g., in Fe- and Co-doped ZnO^{14,15} and Fe in GaN¹⁶). On the other hand, several comprehensive studies on carefully characterized phase-pure materials found only paramagnetism (e.g., in Mn-doped GaN¹⁷ and Co-doped ZnO¹⁸), antiferromagnetic interactions (e.g., in Mn- and Cr-doped GaN^{19,20} and in Co- and Fe-doped ZnO^{21–24}), or at best, ferromagnetic order with very low T_C (e.g., $T_C < 10$ K in Mn-doped GaN²⁵).

On the theoretical side, as the conditions for *p-d* Zener exchange proposed by Dietl *et al.*, i.e., the high concentration of valence-band holes, are generally *not* satisfied in ZnO and GaN, various other models have been proposed.^{26–30} Aiming at describing the observed room temperature ferromagnetism while at the same time accounting for the difficulties in achieving experimental reproducibility, these models share one common characteristic: the presence of lattice defects other than the magnetic impurities, e.g., vacancies, self-interstitials, and grain boundaries. Because the type and concentration of such defects strongly depend on the growth method and conditions and are, in general, difficult to monitor and control, defect-related order mechanisms could, in principle, explain the difficulties in reproducing the ferromagnetic properties. Some models rely on the interplay between such defects and the magnetic impurities, e.g., the bound magnetic polaron (BMP)²⁶ and the charge-transfer ferromagnetism (CTF) models.^{27,28} Others require the presence of only one type of defect, e.g., the spin-split impurity band (SIB) model²⁹ and variants of the BMP model.³⁰ With the development of these models, some experimental evidence has been reported which, although indirectly, supports this picture of defect-related ferromagnetism: by varying the

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defect concentration, it is in some cases possible to turn “on” and “off” the ferromagnetic behavior.^{31–34}

Given the general irreproducibility which characterizes the field, and the limited experimental evidence that DMS materials are intrinsically ferromagnetic at room temperature, significant progress in the field depends on the discovery of a DMS system which is not only ferromagnetic at room temperature but is also simple to prepare and thus easy to reproduce. Among the numerous combinations of materials and preparation methods among which this prototypical DMS could be searched for, the emerging picture of defect-related ferromagnetism seems to point towards disordered systems. In this context, ion implantation may offer a number of advantages compared to doping during growth. Not only it is a relatively simple and highly reproducible process,³⁵ ion bombardment produces a variety of lattice defects, the type and amount of which can be controlled to a certain extent either by tuning the implantation parameters (e.g., target temperature and incident beam energy and angle)^{36,37} or by post-implantation thermal treatment. In addition, as the magnetic dopants can be (randomly) incorporated at low temperature (at least in radiation resistant materials like ZnO and GaN), i.e., below their mobility thresholds, ion implantation may be superior in terms of dopant uniformity and phase purity, both of which are basic conditions to produce an intrinsic DMS. Ion implantation is also the standard doping technique in integrated circuit technology, which would bring ion-implanted *ferromagnetic* DMS materials particularly close to technological implementation. Although not as common as deposition techniques (e.g., pulsed-laser deposition (PLD), metalorganic chemical vapor deposition (MOVPE), and sputter deposition), ion implantation has been used as a doping technique in virtually all of the most intensively studied DMS materials, including Mn-, Fe-, and Co-doped ZnO and GaN (e.g., Refs. 14, 15, and 38–40). However, despite the potential advantages of ion implantation, the irreproducibility in DMS literature extends to ion-implanted systems, with reports of both the presence and absence of room temperature ferromagnetism in virtually identical materials (c.f. Ref. 41 for a recent review).

In this paper, we present an extensive and systematic search for room temperature ferromagnetism in wide-gap DMS systems, using ion implantation as doping method. We focused on the (relatively) low concentration regime ($\sim 0.3\% - 4\%$) in order to minimize phase segregation and varied the major material parameters:

- host wide-gap semiconductors: ZnO and GaN;
- magnetic dopants (3d transition metals): Mn, Fe, and Co;
- dopant concentration: $\sim 0.3\% - 4\%$ by varying fluence ($10^{14} - 10^{16}$ at. cm⁻²) and implantation energy (60–180 keV);
- co-doping with potential electronic dopants in ZnO: Al (donor) and N (acceptor);
- degree of structural disorder: by thermal annealing up to 900°C.

II. EXPERIMENTAL DETAILS: SAMPLE PREPARATION

As host materials, we used commercial ZnO wurtzite [0001] single-crystals (CrysTec GmbH), hydrothermally grown

and Zn-face polished, and high-quality epitaxial GaN [0001] films (2 μm thick), grown on an Al₂O₃ [0001] by metalorganic vapor phase epitaxy (MOVPE).

A. Implantation and annealing parameters

Table I lists the implanted samples and corresponding implantation parameters, as well as the depth-profile parameters simulated using SRIM 2008:⁴² peak concentration x_p with respect to the cation (Zn or Ga) concentration, mean depth (ion range R_p), and depth standard deviation (ion straggle). The sample names are according to the implanted transition metal (“M” for Mn, “F” for Fe, and “C” for Co), fluence in units of 1×10^{14} at. cm⁻², and host compound (“Z” for ZnO and “G” for GaN). A suffix “180” is added for the samples implanted at 180 keV instead of 60 keV. The co-implanted samples are also named according to the co-dopant (“A” for Al and “N” for N). For ZnO, each entry in Table I

TABLE I. Sample list, indicating host material, implanted element, energy, and fluence. The peak concentration (x_p) with respect to the cation (Zn or Ga) concentration, projected ion range (R_p), and ion straggle were estimated using SRIM 2008.⁴²

Sample	Host	Dopant	Energy (keV)	Fluence (at. cm ⁻²)	x_p	R_p (nm)	Straggle (nm)
M5Z	ZnO	Mn	60	5×10^{14}	0.0034	30	14
M10Z	ZnO	Mn	60	1×10^{15}	0.0068	30	14
M50Z	ZnO	Mn	60	5×10^{15}	0.034	30	14
F5Z	ZnO	Fe	60	5×10^{14}	0.0034	29	14
F10Z	ZnO	Fe	60	1×10^{15}	0.0069	29	14
F50Z	ZnO	Fe	60	5×10^{15}	0.034	29	14
C5Z	ZnO	Co	60	5×10^{14}	0.0035	28	13
C10Z	ZnO	Co	60	1×10^{15}	0.0070	28	13
C50Z	ZnO	Co	60	5×10^{15}	0.035	28	13
F10Z180	ZnO	Fe	180	1×10^{15}	0.0027	82	35
F50Z180	ZnO	Fe	180	5×10^{15}	0.013	82	35
F100Z180	ZnO	Fe	180	1×10^{16}	0.027	82	35
M50A50Z	ZnO	Mn	60	5×10^{15}	0.034	30	14
		Al	30	5×10^{15}	0.029	30	15
F50A50Z	ZnO	Fe	60	5×10^{15}	0.034	29	14
		Al	30	5×10^{15}	0.029	30	15
C50A50Z	ZnO	Co	60	5×10^{15}	0.035	28	13
		Al	30	5×10^{15}	0.029	30	15
M50N50Z	ZnO	Mn	60	5×10^{15}	0.034	30	14
		N	17	5×10^{15}	0.028	30	15
F50N50Z	ZnO	Fe	60	5×10^{15}	0.034	29	14
		N	17	5×10^{15}	0.028	30	15
C50N50Z	ZnO	Co	60	5×10^{15}	0.035	28	13
		N	17	5×10^{15}	0.028	30	15
M5G	GaN	Mn	60	5×10^{14}	0.0035	29	13
M10G	GaN	Mn	60	1×10^{15}	0.0070	29	13
M50G	GaN	Mn	60	5×10^{15}	0.035	29	13
F5G	GaN	Fe	60	5×10^{14}	0.0036	28	13
F10G	GaN	Fe	60	1×10^{15}	0.0072	28	13
F50G	GaN	Fe	60	5×10^{15}	0.036	28	13
C5G	GaN	Co	60	5×10^{14}	0.0037	27	13
C10G	GaN	Co	60	1×10^{15}	0.0075	27	13
C50G	GaN	Co	60	5×10^{15}	0.037	27	13

corresponds to two samples, one used for the structural characterization and the other for magnetometry measurements. For GaN, each entry corresponds to 4 samples, i.e., (structural + magnetic characterization) $\times$ (2 different annealing atmospheres).

The main goal of this study is to search for high temperature ferromagnetism under a varying degree of lattice disorder, which can be accomplished by thermal annealing. Annealing of implantation damage in ZnO and GaN is, however, rather complex. The general rule of thumb is that temperatures of around two thirds of the melting point (in units of K) are required to remove extended defects in semiconductors. For ZnO and GaN, this corresponds to about 1200°C (Ref. 43) and 1500–1600°C,^{44,45} respectively. However, in transition metal implanted ZnO and GaN with a peak concentration of $\sim 10\%$ and higher, (undesired) phase segregation occurs already at relatively low annealing temperatures (700–900°C).^{14,15,38–40,46,47} In order to obtain significant damage recovery while avoiding phase segregation, the fluence range and thermal annealing procedure were chosen as follows. The peak-concentration range was limited to $\sim 0.3\% - 4\%$ which, for Mn, Fe, and Co implanted at 60 keV and 180 keV in ZnO and GaN, corresponds to fluences between 5×10^{14} and 1×10^{16} at. cm⁻² (c.f. Table I). After characterization in the as-implanted state, the ZnO and GaN samples were annealed for 10 min in vacuum ($<10^{-5}$ mbar), in steps of 100°C from 300°C to 900°C. Given the tendency for surface decomposition in GaN under vacuum annealing at high temperatures, a separate set of GaN samples were annealed at 900°C for 30 min under N₂ flow, after annealing in vacuum up to 600°C.

B. Al and N co-implantation in transition-metal implanted ZnO

Since transition-metal doped ZnO has also been reported to show room temperature ferromagnetism when co-doped with Al (donor) and N (acceptor) (e.g., Refs. 48–52), a set of ZnO samples implanted with Mn, Fe, or Co to a fluence of 5×10^{15} at. cm⁻² were co-implanted with Al or N, also to a fluence of 5×10^{15} at. cm⁻². Based on SRIM⁴² simulations, the implantation energies were selected in order to maximize the overlap between the transition metal and the Al/N profile (Table I). Note that since we have not characterized these samples in terms of carrier type and concentration, we cannot establish a correlation between activated donor/acceptor concentrations and the presence or absence of high temperature ferromagnetism. In particular, *p*-type doping of ZnO by N-implantation is especially challenging, due to the creation of compensating defects upon ion irradiation (e.g., Ref. 53 and references therein).

III. EXPERIMENTAL DETAILS: CHARACTERIZATION

Magnetic characterization was performed on all samples, in the as-implanted state and following annealing at 300°C, 600°C, and 900°C. The aim of the Rutherford backscattering and channeling spectrometry (RBS/C) measurements was mostly to investigate to what extent the thermal annealing was able to recover the sample crystallinity, i.e., if

the magnetic characterization was indeed performed for a varying level of lattice disorder, from highly disordered to highly crystalline, as desired. Therefore, RBS/C measurements were performed for all annealing steps but only for the highest fluence (for which the beam-induced damage is maximum and the recovery should be minimum compared to the other fluences) of each dopant-compound combination. The set of co-implanted ZnO samples was not characterized by RBS/C, since the relatively low fluence (5×10^{15} at. cm⁻²) of the much lighter (Al and N) co-implants is not expected to considerably change the damage accumulation and annealing behavior. All ZnO samples implanted at 180 keV (three different fluences) were measured by RBS/C.

A. Superconducting quantum interference device (SQUID) magnetometry

The magnetic characterization was performed using a SQUID magnetometer (*Quantum Design* MPMS XL-5) following strict procedures in order to avoid magnetic contamination and other experimental artifacts. These procedures were developed based on statistically relevant tests, which allowed us to determine the practical limits of SQUID magnetometry for the detection of ferromagnetism under various sample preparation, processing, and handling conditions (c.f. Ref. 11 for a detailed description). The measurements were performed with the field perpendicular to the *c*-axis, i.e., parallel to the sample surface.

B. RBS/C

Defect formation and annealing were characterized using RBS/C, with a 1.57 MeV He⁺ beam and two detectors, at backscattering angles of 168° and 105°. The 168° backscattering geometry was used to determine the channeling minimum yield $\chi_{\min}$ along the [0001] axis. The 105° geometry (i.e., with the detector at a 15° glancing exit angle relative to the sample surface) provides a better depth resolution. The minimum yield $\chi_{\min}$ is the ratio ($N_{\text{chan}}/N_{\text{rand}}$) of the backscattering yield with the ion beam aligned with the crystal axis (N_{chan}) to that of random beam incidence (N_{rand}).⁵⁴ As such, $\chi_{\min}$ increases with an increased concentration of atoms which are displaced from ideal substitutional lattice sites, and is therefore a measure of the lattice disorder induced by ion implantation.⁵⁴ For example, high quality single crystals or epitaxial thin films typically have a $\chi_{\min}$ smaller than 0.05, whereas an amorphous layer typically has a $\chi_{\min}$ of ~ 1 .

IV. RESULTS

A. Damage accumulation and annealing

Figures 1(a) and 2(a) show representative RBS/C spectra of unimplanted and implanted ZnO (Fig. 1) and GaN (Fig. 2) samples after different annealing stages, acquired with the 168° backscattering geometry. Figure 1 shows data of sample C50Z (5×10^{15} cm⁻² Co-implanted ZnO); the data are similar for Mn and Fe. Figure 2 shows data of sample M50G (5×10^{15} cm⁻² Mn-implanted GaN); the data are similar for Fe and Co. As typical for ZnO⁵⁵ and GaN,⁵⁶ lattice disorder in the Zn/Ga sublattice accumulates in two regions: in the

FIG. 1. (a) RBS/C spectra acquired with the 168° backscattering geometry: channeling spectra of an unimplanted ZnO sample and sample C50Z ($5 \times 10^{15} \text{ cm}^{-2}$ Co-implanted ZnO) after different annealing stages, compared to the random spectrum of the unimplanted sample. The dashed line separates the surface and bulk energy windows used to calculate the corresponding $\chi_{\min}$. (b) RBS/C spectra acquired with the 105° geometry (15° glancing exit angle): channeling spectra of the same sample C50Z and same annealing stages as in (a). The arrow indicates the position of the MDP region.

crystal bulk (bulk peak), where the energy loss is maximum; and near the sample surface (surface peak), which acts as a sink for mobile defects created by the ion bombardment. This bimodal damage accumulation is particularly clear in the spectra measured in glancing-angle detector geometry, with higher depth resolution [Figs. 1(b) and 2(b)]. It is also particularly clear in the Fe:ZnO implanted at 180 keV [Fig. 3(a)], where the Fe profile reaches deeper in the sample and the surface and bulk regions are thus better resolved in the RBS/C spectra. The channeling minimum yield $\chi_{\min}$ is, therefore, determined separately for the two regions, i.e., surface and bulk, from the RBS/C spectra in 168° backscattering geometry. Bulk $\chi_{\min}$ values are compiled in Fig. 4(a) and surface $\chi_{\min}$ values in Fig. 4(b) for the three transition metal dopants in ZnO, as a function of annealing temperature up to 900°C. Similarly bulk $\chi_{\min}$ and surface $\chi_{\min}$ values are compiled in Fig. 5 for GaN.

The overall behavior is similar for both host materials and for all three transition metal dopants (Mn, Fe, and Co). Both ZnO and GaN remain crystalline even after a relatively high fluence implantation ($5 \times 10^{15} \text{ cm}^{-2}$), as the backscattering yield in the as-implanted state is well below the random level (which would correspond to amorphization). This reflects the efficient *dynamic annealing* which characterizes ZnO and GaN and is responsible for its known high radiation

FIG. 2. (a) RBS/C spectra acquired with the 168° backscattering geometry: channeling spectra of an unimplanted GaN sample and sample M50G ($5 \times 10^{15} \text{ cm}^{-2}$ Mn-implanted GaN) after different annealing stages, compared to the random spectrum of the unimplanted sample. The dashed line separates the surface and bulk energy windows used to calculate the corresponding $\chi_{\min}$. (b) RBS/C spectra acquired with the 105° geometry (15° glancing exit angle): channeling spectra of the same sample M50G and same annealing stages as in (a).

resistance. Still, significant lattice disorder is induced upon implantation in the end of range (EOR) region, corresponding to the bulk $\chi_{\min}$ ($> 50\%$), which in turn is significantly recovered upon thermal annealing, with the main difference between ZnO and GaN being the temperature range at which the major recovery starts (600°C in ZnO and 700°C in GaN). These and other differences are discussed next as we analyze the damage build-up and annealing for ZnO and GaN separately.

1. ZnO

The most important observation with regards to the main purpose of this work, i.e., searching for ferromagnetism under a varying degree of crystallinity, is that thermal annealing progressively decreases the bulk $\chi_{\min}$ (i.e., the relative disorder in the region of interest, the dopant EOR region) from highly disordered (40%–50%) in the as-implanted state to virtually perfectly crystalline after 900°C annealing (3%–5%), similar to the unimplanted sample (3%) [Fig. 4(a)]. It is also important to note that no major differences can be observed between the three different transition metal impurities. For the samples implanted at 180 keV (Fig. 6), $\chi_{\min}$ increases with implanted fluence as expected, and the annealing behavior is virtually the same as for the samples implanted at 60 keV.

FIG. 3. (a) RBS/C spectra acquired with the 168° backscattering geometry: channeling spectra of an unimplanted ZnO sample and sample F50Z180 ($5 \times 10^{15} \text{ cm}^{-2}$ Fe-implanted ZnO at 180 keV) after different annealing stages, compared to the random spectrum of the unimplanted sample. The dashed line separates the surface and bulk energy windows used to calculate the corresponding $\chi_{\min}$. (b) RBS/C spectra acquired with the 105° geometry (15° glancing exit angle): channeling spectra of the same sample F50Z180 and same annealing stages as in (a). The arrow indicates the position of the MDP region.

Looking in somewhat more detail at the evolution of the damage in the bulk region upon annealing, it appears that for all three transition metals [Fig. 1(b) for Co] the damage in the EOR region survives annealing up to higher temperatures compared to the region between the EOR and the surface. This can be attributed to trapping of lattice defects (such as vacancies and self-interstitials) by the transition-metal impurities.

Another interesting feature of the ZnO spectra is the appearance of a third damage peak, between the common surface and bulk peaks (indicated by arrows in Figs. 1 and 3). This *middle defect peak* (MDP) was also observed in Au-implanted ZnO by Kucheyev *et al.*,⁵⁵ where it was attributed to a localized band of lattice defects, which nucleates in the near surface region due to incomplete dynamic annealing during ion bombardment. This, in turn, is likely to result from the spatial separation between vacancies and interstitials in the collision cascades, which creates an excess of vacancies closer to the surface and an excess of interstitials near the EOR region. The MDP is particularly well resolved in the samples implanted with Fe with an energy of 180 keV [Fig. 3(b)], as the bulk and surface regions are better resolved, which shows in addition that the MDP-related damage is annealed at 700°C.

FIG. 4. (a) Bulk and (b) surface $\chi_{\min}$ of samples M50Z, F50Z, and C50Z, i.e., $5 \times 10^{15} \text{ cm}^{-2}$ Mn-, Fe-, and Co-implanted ZnO, respectively, as a function of annealing temperature. The dashed line corresponds to the $\chi_{\min}$ of an unimplanted and non-annealed ZnO sample.

2. GaN

Not only is $\chi_{\min}$ higher in as-implanted GaN (53%–55%) [Fig. 5(a)] than in ZnO (41%–49%) [Fig. 4(a)], major recovery also only starts at higher temperatures (700°C in GaN compared to 600°C in ZnO). In addition, thermal annealing is less efficient in recovering the crystallinity of GaN. Annealing in vacuum up to 900°C results in a bulk $\chi_{\min}$ of 8%–23%, considerably higher than for ZnO (bulk $\chi_{\min}$ of 3%–5%). Annealing in N_2 flow is more efficient (bulk $\chi_{\min}$ of 7%–10%, although still significantly higher than the 2.5% prior to implantation).

The higher degree of beam-induced disorder in GaN compared to ZnO is even more noticeable in the surface region, with GaN showing a higher surface $\chi_{\min}$ from the as-implanted state up to the last annealing step [Fig. 5(b)]. This is also visible in the RBS/C spectra measured in glancing-angle detector geometry [Fig. 2(b)], with a surface peak which is more intense than the bulk peak, as opposed to the ZnO case [Fig. 1(b)]. The difference between host materials is consistent with the lower surface amorphization threshold observed by Kucheyev *et al.* in GaN⁵⁶ compared to ZnO,⁵⁵ which is probably associated with a higher tendency for N loss in the GaN surface upon ion bombardment, compared to O loss in ZnO. The trapping of native defects by the implanted impurities, discussed above for ZnO, can also be inferred from the GaN data.

FIG. 5. (a) Bulk and (b) surface $\chi_{\min}$ of samples M50G, F50G, and C50G, i.e., $5 \times 10^{15} \text{ cm}^{-2}$ Mn-, Fe-, and Co-implanted GaN, respectively, as a function of annealing temperature. Full symbols correspond to vacuum annealing; open symbols correspond to annealing in N_2 flow. The dashed line corresponds to the $\chi_{\min}$ of an unimplanted and non-annealed GaN sample.

B. Magnetic characterization

Figure 7(a) shows $\mu(H)$ data (magnetic moment μ as a function of applied magnetic field H) measured at 300 K, dominated by the diamagnetic susceptibility of the ZnO substrate (similar for the GaN grown on Al_2O_3 substrates). Since, to a good approximation, the diamagnetic susceptibility χ_{dia} of ZnO and Al_2O_3 does not depend on the applied field, one can search for a possible residual ferromagnetic-like component by estimating χ_{dia} from the linear fit of the data between 1 and 2 T, where the ferromagnetic component is, in principle, saturated, and plotting $(\mu(H) - \chi_{\text{dia}}H)$. Examples of such residual signals are shown in Fig. 7(b) for the samples which showed the lowest $(7(5) \times 10^{-8} \text{ emu})$ and highest $(5.2(5) \times 10^{-7} \text{ emu})$ saturation moment. We have shown in Ref. 11 that such residual ferromagnetic-like signals with a saturation moment smaller than $5 \times 10^{-7} \text{ emu}$ can be attributed to magnetic contamination or measurement artifacts. Most of the samples in the present study had a saturation moment in that range, i.e., did not exhibit ferromagnetic behavior (at 300 K) above the experimental detection limit. For the few samples which did, we implanted new samples under the same conditions. This second set of samples had saturation magnetization below $5 \times 10^{-7} \text{ emu}$, with the exception of $5 \times 10^{15} \text{ cm}^{-2}$ Fe-implanted ZnO (F50Z); a third F50Z sample was prepared, which showed a saturation

FIG. 6. (a) Bulk and (b) surface $\chi_{\min}$ of samples F10Z180, F50Z180, and F100Z180, i.e., Fe-implanted ZnO (180 keV implantations) to fluences of $1 \times 10^{15} \text{ cm}^{-2}$, $5 \times 10^{15} \text{ cm}^{-2}$, and $1 \times 10^{16} \text{ cm}^{-2}$, respectively. The dashed line corresponds to the $\chi_{\min}$ of an unimplanted and non-annealed ZnO sample.

moment below 5×10^{-7} . In addition, all samples that showed a saturation moment above 5×10^{-7} at some annealing stage were cleaned using the protocol described in Ref. 11. After the cleaning procedure, the saturation moment of all the samples decreased significantly, most of them to below $5 \times 10^{-7} \text{ emu}$. The saturation moment of samples C50Z and M50G, representative of all other samples, is plotted in Fig. 8 as a function of annealing temperature. The slight increase in saturation moment with increasing annealing temperature reflects the increase in number of processing steps, i.e., of contaminating events. We conclude that none of the samples showed intrinsic ferromagnetism above the experimental detection limit; the ferromagnetism observed in some samples can be attributed to magnetic contamination, as extensively discussed in Ref. 11. However, one cannot exclude that the residual hystereses are at least partially due to intrinsic ferromagnetism induced by the magnetic doping. Table II lists the maximum ferromagnetic saturation moment per implanted transition metal atom consistent with a detection limit of $5 \times 10^{-7} \text{ emu}$ for samples with a surface area of approximately $5 \times 5 \text{ mm}^2$.

V. DISCUSSION

Despite the wide range of implantation and post-processing conditions, none of the impurity-host combinations showed measurable room-temperature ferromagnetism.

FIG. 7. Examples of (a) $\mu(H)$ data as measured at 300 K (sample C50Z) and (b) ferromagnetic-like component obtained by subtracting the linear component estimated between 1 and 2 T (sample C50Z as implanted ($\bullet$) and sample M50Z following 900°C annealing ($\circ$)). All data were measured in decreasing field (2 T to -2 T). The gray region indicates the range corresponding to magnetic contamination and instrumental limits as established in a previous study.¹¹

In particular, even though we covered a wide range of density of beam-induced damage by varying the implanted fluence and the annealing temperature, no sign of defect-related ferromagnetism could be observed. This strongly supports the view that the high temperature ferromagnetism often reported in ZnO and GaN can be attributed to magnetic contamination (as observed here) and to ferromagnetic secondary phases (as demonstrated for example in Refs. 14, 15, 38–40, 46, and 47).

This absence of high temperature ferromagnetism raises an important question: what is then the magnetic behavior of these materials? We have not addressed this here, but a number of comprehensive reports exist on individual wide-gap DMS materials either doped during growth or by ion implantation (e.g., Fe- and Co-doped ZnO^{18,21–24} and Mn- and Cr-doped GaN^{17,19,20}) which seem to provide a general and rather consistent answer. For sufficiently low concentrations, the isolated transition-metal impurities, the large majority of which are located on cation-substitutional sites,^{57–60} behave as localized paramagnetic moments.^{17,18,20} With increasing concentration and the consequent decrease of the mean distance between the impurities in the lattice, this paramagnetism is affected by strong *antiferromagnetic* interactions between the localized magnetic moments of nearest-cation-neighbor impurities.^{19–24} The dominance of antiferromagnetic over ferromagnetic interactions between nearest-cation-neighbor

FIG. 8. Examples of the saturation moment of the ferromagnetic-like component of the $M-H$ data as a function of annealing temperature, for (a) samples M50Z, F50Z, and C50Z ($5 \times 10^{15} \text{ cm}^{-2}$ Mn-, Fe-, and Co-implanted ZnO, respectively) and (b) samples M50G, F50G, and C50G ($5 \times 10^{15} \text{ cm}^{-2}$ Mn-, Fe-, and Co-implanted GaN, respectively). Open symbols correspond to vacuum annealing and full symbols to annealing in N_2 flow. The gray region indicates the range corresponding to magnetic contamination and instrumental limits.¹¹

transition metals in oxides and nitrides can hardly be considered surprising, since most transition-metal oxides and nitrides are indeed antiferromagnetic. On the other hand, the proposed mechanisms of longer-ranged ferromagnetic interactions between transition metal impurities depend on conditions which are not necessarily satisfied in wide-gap DMS materials. Transition metals form deep levels in the ZnO and GaN bandgap and therefore do not introduce the p -holes required to mediate ferromagnetic $p-d$ Zener interaction. Regarding BMP models, the exchange energy density necessary to produce high-temperature ferromagnetism with a few percent of transition-metal doping corresponds to a magnetic

TABLE II. Maximum magnetic moment per implanted transition-metal atom μ_{at} , in case the observed residual hystereses (with a saturation moment of the order of $5 \times 10^{-7} \text{ emu}$) would originate from intrinsic, doping-related ferromagnetism.

Fluence [at. cm^{-2}]	μ_{at} [μ_B]
5×10^{14}	0.43
1×10^{15}	0.22
5×10^{15}	0.043
1×10^{16}	0.022

exchange much stronger than that observed in the strongest of the known ferromagnetic materials.²⁸ Other mechanisms have been proposed which do not rely on ordered 3d local moments and Heisenberg-type exchange as in *p-d* Zener exchange and BMP models. For example, the CTF model,²⁸ a Stoner-type mechanism, requires two distinct types of defects, one that creates a narrow impurity band and another to play the role of charge reservoir. However, it remains to be demonstrated if such a type of defect does exist which creates an impurity band that can be spontaneously spin-split. In particular, based on our results presented here and in Ref. 20 (for Cr-implanted GaN), beam-induced defects do not seem to satisfy those requirements.

VI. CONCLUSIONS

In summary, none of the wide-gap DMS layers prepared by ion implantation of Mn, Fe, and Co in ZnO and GaN showed measurable room temperature ferromagnetism. Given the wide range of material, implantation and post-processing parameters covered in this study, our findings indicate that transition-metal implanted ZnO and GaN are not ferromagnetic at room temperature. In agreement with recent comprehensive reports of the absence of ferromagnetism in wide-gap DMS prepared by various other methods, these results support the view that dilute transition-metal moments do not order ferromagnetically in ZnO and GaN. In addition, this work demonstrates the importance of proper procedures to avoid extrinsic sources of ferromagnetism, such as ferromagnetic contamination and instrumental artifacts.

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