Fe implanted ZnO: magnetic precipitates versus dilution

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Nowadays ferromagnetism is often found in potential diluted magnetic semiconductor systems. However, many authors argue that the observed ferromagnetism stems from ferromagnetic precipitates or spinodal decomposition rather than from carrier mediated magnetic impurities, as required for a diluted magnetic semiconductor. In the present paper we answer this question for Fe-implanted ZnO single crystals comprehensively. Different implantation fluences and temperatures and post-implantation annealing temperatures have been chosen in order to evaluate the structural and magnetic properties over a wide range of parameters. Three different regimes with respect to the Fe concentration and the process temperature are found: 1) Disperse Fe$^{2+}$ and Fe$^{3+}$ at low Fe concentrations and low processing temperatures, 2) FeZn$_2$O$_4$ at very high processing temperatures and 3) an intermediate regime with a co-existence of metallic Fe (Fe$^0$) and ionic Fe (Fe$^{2+}$ and Fe$^{3+}$). Ferromagnetism is only observed in the latter two cases, where inverted ZnFe$_2$O$_4$ and α-Fe nanocrystals are the origin of the observed ferromagnetic behavior, respectively. The ionic Fe in the last case could contribute to a carrier mediated coupling. However, their separation is too large to couple ferromagnetically due to the lack of p-type carrier. For comparison investigations of Fe-implanted epitaxial ZnO thin films are presented.

I. INTRODUCTION

Recently, considerable interest has been paid to "spintronics", where the spin degree of freedom of the electron carries information in the device. One of the material systems to realize this function are diluted magnetic semiconductors (DMS). In DMS materials, transition or rare earth metal ions are substituted onto cation sites and are coupled with the free carriers to yield ferromagnetism via indirect interaction. In 2000, Dietl et al. [1] proposed the mean-field Zener model to understand the ferromagnetism in DMS materials. It has been successfully used to describe the magnetic coupling in (Ga,Mn)As and (Zn,Mn)Te materials. This model predicts that wide bandgap semiconductors (GaN and ZnO) doped with Mn exhibit ordering temperatures above 300 K, provided that a sufficiently large hole density can be achieved ($10^{20}$ cm$^{-3}$). Sato et al. used the Körringa-Kohn-Rostoker Green function method based on the local density approximation of density functional theory to calculate the properties of n-type ZnO doped with the 3d TM ions (V, Cr, Mn, Fe, Co, and Ni) [2]. The ferromagnetic state, with a $T_C$ of around 2000 K, is predicted to be favourable for V, Cr, Fe, Co, and Ni in ZnO while Mn-doped ZnO is antiferromagnetic. These predictions have largely boosted intensive experimental activity on transition metal doped GaN and ZnO. A large number of research groups reported the experimental observation of ferromagnetism in TM (from Sc to Ni) doped ZnO fabricated by various methods including ion implantation. In contrast to these results, other groups reported the observations of antiferromagnetism spin-glass behavior in TM-doped ZnO. Recently it was also found that nanoscale precipitates can substantially contribute to the ferromagnetic properties. One method to introduce magnetic dopants into ZnO is ion implantation. It has several advantages, namely the reproducibility, the precise control of the ion fluence, the use of an isotopically pure beam, and the possibility to overcome the solubility limit. The major drawback of ion implantation is the generation of structural defects in the host lattice. However, in several studies it has been demonstrated that ZnO exhibits a high amorphization threshold. Therefore ion implantation is widely used to dope ZnO with transition metal ions. Ref. [28] gives a review on transition metal ion implantation into ZnO.

Hydrothermal growth is one of the major methods to fabricate high quality ZnO single crystals [29-31]. Hydrothermal grown ZnO single crystals have been widely used for photodiodes [31], light emitters [32], DMS [23,33-34], and substrates for homoepitaxial growth of ZnO films [35].

The present paper is dedicated to a comprehensive investigation of the structural and magnetic properties of Fe implanted ZnO bulk crystals grown by the hydrothermal method. Different implantation parameters, i.e. ion fluence, ion energy, and implantation temperature, were varied. Three charge states or occupied sites, i.e. metallic

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Fe and monodispersed Fe\(^{2+}\) and Fe\(^{3+}\) in Zn-ferrites, are identified. Metallic Fe nanocrystals (NCs) form after implantation at high fluence and high temperature. They are the major contribution to the measured ferromagnetism. The difference between ZnO single crystals and epitaxial thin films upon the same implantation, and the difference between the high (623 K) and the low (253 K) temperature implanted samples subject to the same annealing, will be discussed.

Actually the phase separation, namely MnAs precipitates, in (Ga,Mn)As (the most well understood DMS material), has been extensively investigated [36]. Ferromagnetic MnAs precipitates are epitaxially embedded inside the GaAs matrix, and exhibit interesting magneto-transport properties [37][38][39][40]. Sato and Katayama-Yoshida [41][42] calculated the chemical pair interaction between two magnetic impurities in DMS materials. A strong attractive interaction between magnetic impurities has been found, which accelerates the spinodal nano-decomposition under thermal non-equilibrium crystal growth conditions. Moreover the attractive interaction in (Ga,Mn)As is one order of magnitude weaker than that in (Ga,Mn)N (wide bandgap semiconductor). Therefore, phase separation in TM doped wide bandgap semiconductors is highly expected. In addition to these investigations of MnAs/GaAs hybrids, some interesting magneto-transport properties are demonstrated, e.g. anomalous hall effect, and giant magnetoresistance, for magnetic NCs embedded inside ZnS [43] and Ge [44], respectively. Therefore, Fe NCs embedded inside ZnO, which are granular magnetic nano-precipitates inside a semiconductor (granular magnetic semiconductor, GMS), could have some potential applications in future nano-spintronics [42][43].

The paper is organized as follows. First, all the experimental methods employed will be described. Then the results will be separated according to the physical phenomena as follows: lattice damage and recovering, the distribution of implanted Fe, the formation of precipitates (metallic Fe, or Fe-ferrites), the charge state of Fe, the ferromagnetic properties, and the Fe implanted epitaxial ZnO films. In the discussion part, we sketch a phase diagram of Fe in ZnO, and apply a model to explain the Fe nanocrystal aggregation. Moreover the reason for the absence of ferromagnetism in ionic Fe diluted ZnO is discussed.

II. EXPERIMENTS

Commercial ZnO bulk crystals were implanted with \(^{57}\)Fe ions at temperatures ranging from 253 K to 623 K with fluences from 0.1 \times 10^{16} \text{ cm}^{-2} to 8 \times 10^{16} \text{ cm}^{-2}. The implantation energy was 180 keV, which results in a projected range of \(R_P = 89 \pm 29 \text{ nm}\), and a maximum atomic concentration from 0.14\% to 11\% (TRIM code [46]). For comparison, epitaxial ZnO thin films grown on Al\(_2\)O\(_3\) by pulsed laser deposition were implanted with \(^{57}\)Fe at selected implantation parameters (623 K, 4 \times 10^{16} \text{ cm}^{-2}). Three sample series are investigated and listed in Table II.

The lattice damage induced by implantation was evaluated by Rutherford backscattering/channeling spectroscopy (RBS/C). The RBS/C spectra were collected with a collimated 1.7 MeV He\(^+\) beam at a backscattering angle of 170\(^\circ\). The sample was mounted on a three-axis goniometer with a precision of 0.01\(^\circ\). The channeling spectra were collected by aligning the sample to make the impinging He\(^+\) beam parallel with the ZnO<0001> axis. \(\chi_{\text{min}}\) is the channeling minimum yield in RBS/C, which is the ratio of the backscattering yield at channeling condition to that for a random beam incidence [47]. Therefore, \(\chi_{\text{min}}\) labels the lattice disordering degree upon implantation. An amorphous sample exhibits a \(\chi_{\text{min}}\) of 100\%, while a perfect single crystal corresponds to a \(\chi_{\text{min}}\) of 1-2\%.

The Fe distributions were investigated by secondary ion mass spectrometry (SIMS), using a Riber MIQ-256 system with oxygen primary ions of 6 kV and monitoring positive secondary ions. The depth scale was calibrated by measuring the sputtered crater via profilometry. The absolute concentration was determined by calculating the sensitivity factors from the low fluence implants.

Structural analysis was achieved both by synchrotron radiation x-ray diffraction (SR-XRD) and conventional XRD. SR-XRD was performed at the Rossendorf beamline (BM20) at the ESRF with an x-ray wavelength of 0.154 nm. 2θ-θ scans were used to identify crystalline precipitates.

Conversion electron Mössbauer spectroscopy (CEMS) in constant-acceleration mode at room temperature (RT) was used to investigate the Fe lattice sites, electronic configuration and corresponding magnetic hyperfine fields. The spectra were evaluated with Lorentzian lines using a least squares fit [48]. All isomer shifts are given with respect to \(\alpha\)-Fe at RT.

The magnetic properties were measured with a superconducting quantum interference device (SQUID, Quantum Design MPMS) magnetometer in the temperature range of 5-350 K. The samples were measured with the field aligned either along the in- or out-of-plane direction. The temperature dependence of the magnetization was studied at a constant field and the field dependence at a constant temperature. By magnetic measurement, virgin ZnO is found to be purely diamagnetic with a susceptibility of -2.65 \times 10^{-7} \text{ emu/Oe}. This background was subtracted from the magnetic data. To measure the temperature dependent magnetization after zero field cooling and field cooling (ZFC/FC), the sample was cooled in zero field from above room temperature to 5 K. Then a 50 Oe field was applied. The ZFC curve was measured with increasing temperature from 5 to 300 (or 350) K, after which the FC curve was measured in the same field from 300 (or 350) to 5 K with decreasing temperature.
FIG. 1: (a) Representative RBS random and channeling spectra of Fe implanted ZnO with the implantation energy of 180 keV. The fluence is indicated on the channeling spectra. The dashed line separates the damage regions of surface and bulk, where the number of displaced atoms is maximum. (b) The ion fluence dependence of the maximum relative disorder of the Zn lattice ($\chi_{\text{min}}$) at different depth (surface and bulk).

III. RESULTS

In this section, we present experimental data on structural and magnetic properties of $^{57}$Fe implanted ZnO. Of interest in this study are the ion-implantation induced lattice damage, the distribution of Fe, the formation of metallic Fe nanocrystals, the charge state of Fe, the magnetic properties, and the structure and magnetism evolution upon post annealing. The difference between ZnO bulk crystals and epitaxial films upon Fe implantation is also compared.

A. Lattice damage accumulation

1. Fluence dependence

Figure 1(a) shows representative RBS/C spectra for different Fe fluences implanted at 623 K. The arrow labelled Zn indicates the energy for backscattering from surface Zn atoms. The implanted Fe ions cannot be detected for the lowest fluence ($0.1 \times 10^{16}$ cm$^{-2}$). However, they are more pronounced as a hump in the random spectrum for a high fluence of $8 \times 10^{16}$ cm$^{-2}$. The channeling spectrum of a virgin sample is provided for comparison. The yield increase in the channeling spectra mainly originates from the lattice damage due to implantation. However, in the higher fluence case, the Fe ions also significantly increase the RBS yields. Two features are observed in the RBS/C spectra. One is the bimodal distribution of maximum damage depths, i.e., in the bulk and at the surface, separated by the dashed line in Figure 1(a). Similar depth profiles have already been discussed by Kucheyev et al. In the bulk damage region the nuclear energy-loss profile is maximum, which induces a large number of atomic displacements. The surface damage peak is often a sink for ion implantation induced point defects.

Another feature is the saturation at larger fluences. $\chi_{\text{min}}$, the ration of the channeling spectrum to the random one, is calculated in both damage regions, as shown in Figure 1(b). Above a fluence of $2 \times 10^{16}$ cm$^{-2}$, both damage peaks saturate. This is due to the strong dynamic annealing effect, i.e., migration and interaction of defects during ion implantation. This strong dynamic annealing also makes ZnO an irradiation-hard material, i.e., it still partly persists a crystalline state after irradiation by Fe ions up to a fluence of $8 \times 10^{16}$ cm$^{-2}$ ($\chi_{\text{min}}$ of 68%).

2. Implantation temperature dependence

In general increasing the substrate temperature during implantation can suppress the lattice damage in semiconductors. However, this is not the case for ZnO. Figure 2(a) shows the channeling spectra for Fe implanted ZnO at different implantation temperatures. Although the surface damage peak increases drastically with decreasing implantation temperature, the bulk damage peak is hardly affected by implantation temperature. This can be observed clearly in Figure 2(b). The point defects induced by ion-beam can be significantly suppressed by increasing the implantation temperature above 623 K. This temperature is very critical, and below 623 K, the surface damage peak also has no dependence on the substrate temperature. This is very important for the electrical doping of ZnO by ion implantation, where point defects are believed to decrease the conductivity.

3. Recovering by post-annealing

As shown above, the bulk damage cannot be suppressed by increasing the implantation temperature. It has to be removed by post annealing at higher temperature. The annealing was performed in high vacuum in order to avoid extrinsically induced oxidation of Fe. The
temperature was varied from 823 K to 1073 K. The details have been reported in the Ref. [27]. Both the surface and bulk damage peaks decreased progressively with increasing the annealing temperature and time. However even after annealing at 1073 K for 3.5 hours, there is still considerable damage. This is because of the high melting point of ZnO (∼2250 K). The extended defects can only be removed completely by annealing at approximately two-thirds of the melting temperature [51]. Therefore a high annealing temperature (1500 K) is necessary to completely recover the lattice structure of ZnO. However, high vacuum annealing above 1000 K also lead the decomposition of ZnO [52].

B. Fe distribution

RBS/C can give an overview of the lattice damage upon Fe implantation. However, since the mass of Fe is smaller than Zn, it is difficult to obtain the depth profile of the implanted Fe. Therefore, SIMS is employed to determine the Fe depth profile (see Figure 3(a)). It is observed that the peak concentration of Fe increases from 0.1% to 7%, with a projected range of \( R_P = (80-90) \pm (20-30) \). This is in a rather good agreement with TRIM simulations [46]. The only discrepancy is the high fluence sample \( (4 \times 10^{16} \text{ cm}^{-2}) \), where TRIM simulations predict a peak concentration of 5%. This is due to the change in SIMS sensitivities for different materials, which implies that the determined concentrations are more accurate in the low concentration (below 1%) regime.

In Figure 3(b) the Fe depth profile is compared for different temperatures with the same fluence of \( 4 \times 10^{16} \text{ cm}^{-2} \). The profile does not change significantly due to elevating the implantation temperature from 253 K to 623 K. The slightly higher concentration for implantation at 253 K is within the fluence error.

As discussed in Ref. [27], Fe diffuses towards the surface after high temperature annealing. The same diffusion of Fe upon annealing was also observed by SIMS (not shown).
FIG. 4: SR-XRD 2θ-θ scans of Fe implanted ZnO for different fluences reveal the formation of crystalline Fe nanoparticles.

C. Formation of Fe NCs

By employing SR-XRD, we have systematically investigated the formation of Fe NCs, and its dependence on the fluence and implantation temperature by SR-XRD.

1. Fluence dependence

Figure 4 shows the SR-XRD pattern (focused on Fe(110) peak) as a function of fluence. At a low fluence ($0.1 \times 10^{16}$ to $0.8 \times 10^{16}$ cm$^{-2}$), no crystalline Fe NCs could be detected, while above a fluence of $2 \times 10^{16}$ cm$^{-2}$, an Fe(110) peak appears and increases with fluence. The inset shows a wide range scan for the high fluence sample ($4 \times 10^{16}$ cm$^{-2}$). No other Fe-oxide ($\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, and $\text{ZnFe}_2\text{O}_4$) particles are detected in the as-implanted state. The full width at half maximum (FWHM) of the Fe(110) peak decreases with fluence, indicating a growth of the average diameter of these NCs. The crystallite size is calculated using the Scherrer formula [53].

$$d = 0.9\lambda/(eta \cdot \cos \theta)$$  \hspace{1cm} (1)

where $\lambda$ is the wavelength of the x-ray, $\theta$ the Bragg angle, and $\beta$ the FWHM of $2\theta$ in radians. The crystallite size was estimated using Eq. 1 and is listed in Table I.

Note, that only one peak of Fe(110) appears in the inset of Figure 4. This indicates a texture of the Fe NCs. However no texture behavior is found even for the highest fluence sample in pole figure measurements on Fe(110) and Fe(200) (not shown). This could be due to the difference in the crystalline symmetry of hexagonal ZnO (six fold symmetry) and bcc-Fe (four fold symmetry). For a bcc-crystal, one cannot find a six-fold symmetry viewed from any direction. In contrast, hcp-Co(0001) and fcc-Ni(111) NCs, which are six-fold symmetric, are found to be crystallographically oriented inside ZnO matrix. This highly ordered orientation allows them to be detected even by laboratory XRD [26][54].

2. Implantation temperature dependence

SR-XRD was also performed for the samples with an Fe fluence of $4 \times 10^{16}$ cm$^{-2}$ implanted at different temperatures from 253 K to 623 K. As shown in Figure 5, for implantation temperatures of 473 K and below, no crystalline Fe could be detected. This is also confirmed by the CEMS results (shown later), where the Fe$^0$ state appears only at an implantation temperature of 623 K. Note the asymmetry of the ZnO(0002) diffraction peaks in Figure 5. Shoulders on the right side (smaller lattice constant) are clearly observed. These shoulders decrease with increasing implantation temperature, and can therefore be associated with lattice damage or ZnO substituted with Fe. In view of a detailed study of ion implantation into GaN where the implantation induces a lattice expansion of GaN (a shoulder at left side) [55][56], we rather attribute the observed right side shoulders to ZnO substituted with Fe. In the 623 K implantation, metallic Fe NCs start to form, therefore the substitution is reduced.

3. Growth with post-annealing

After thermal annealing at 823 K for 15 min, more α-Fe NCs of a larger size are formed for the samples implanted at 623 K. After 1073 K and 15 min annealing, the α-Fe almost disappears and $\text{ZnFe}_2\text{O}_4$ starts to form. The details of the structure and magnetism evolution upon thermal annealing can be found in the Ref. [27].
TABLE I: Structural properties of $^{57}$Fe-implanted ZnO bulk crystals and epitaxial thin films. The implantation energy is 180 keV.

| Fluence (cm$^{-2}$) | Implantation Temperature (K) | Peak Concentration (TRIM simulation) | Peak Concentration (SIMS) | $\chi_{\text{min}}$ (RBS/C) | Metallic Fe Formation |
|-------------------|-----------------------------|-------------------------------------|---------------------------|-----------------------------|----------------------|
| $0.1 \times 10^{16}$ | 623 | 0.14% | 0.1% | 8.1% | 5.9% | No |
| $0.4 \times 10^{16}$ | 623 | 0.55% | 0.46% | 38% | 14% | No |
| $0.8 \times 10^{16}$ | 623 | 1.1% | 0.89% | 43% | 16% | No |
| $2 \times 10^{16}$ | 623 | 2.7% | 2.6% | 57% | 39% | $\alpha$-Fe |
| $4 \times 10^{16}$ | 623 | 5.5% | 6.0% | 60% | 32% | $\alpha$-Fe |
| $8 \times 10^{16}$ | 623 | 11% | - | 65% | 55% | $\alpha$-Fe |
| $0.4 \times 10^{16}$ | 253 | 0.55% | 0.5% | 31% | 16% | No |
| $4 \times 10^{16}$ | 253 | 5.5% | 5.5% | 65% | 43% | No |
| $4 \times 10^{16}$ | 298 | 5.5% | - | 65% | 40% | No |
| $4 \times 10^{16}$ | 473 | 5.5% | - | 66% | 42% | No |
| $4 \times 10^{16}$ | 623 K | 5.5% | - | 44% | - | $\alpha$ and $\gamma$-Fe |

$^a$ZnO epitaxial thin films.

TABLE II: Structural and magnetic properties for Fe-implanted ZnO. The ferromagnetic fraction corresponds to the percentage of ferromagnetic Fe (at 5 K) compared with all implanted Fe ions. The crystallite size evaluated by ZFC magnetization is only for $\alpha$-Fe NCs.

| Fluence (cm$^{-2}$) | Sample T$_{\text{emp.}}$ (K) | Sample T$_{\text{ann.}}$ (K) | Crystallite size (XRD) (nm) | $T_B$ (ZFC) (K) | Crystallite size (ZFC) (nm) | Saturation magnetization (5 K) (µ$_B$/Fe) | Ferromagnetic Fe fraction $^b$ (%) | Coercivity at 5 K (Oe) |
|-------------------|-----------------------------|-----------------------------|---------------------------|----------------|---------------------------|-----------------------------|-----------------|----------------|
| $2 \times 10^{16}$ | 623 | - | 5.6 | 38 | 8 | 6.6 | 0.08 | 3.6 | 600 |
| $4 \times 10^{16}$ | 623 | - | 7.1 | 137 | 12 | 8.9 | 0.24 | 11 | 360 |
| $8 \times 10^{16}$ | 623 | - | 8.9 | 212 | 14 | 11.3 | 0.13 | 5.9 | 360 |
| $4 \times 10^{16}$ | 623 | 823 | 9.4 | 200 | 14 | 10.2 | 0.34 | 15 | 360 |
| $4 \times 10^{16}$ | 253 | 823 | - | 295 | 16 | 9.5 | 0.52 | 24 | 370 |
| $4 \times 10^{16}$ | 623 | - | -/6 ($\alpha$/γ-Fe) | 26 | 7 | 4.6 | 0.55 | 25 | 220 |
| $4 \times 10^{16}$ | 623 | 823 | 8.1/11 ($\alpha$/γ-Fe) | 280 | 15 | 10.2 | 1.3 | 59 | 220 |

$^a$ZnO epitaxial layers implanted with Fe at 180 keV and 623 K.
$^b$Calculated by comparing the saturation magnetization with the value (2.2 µ$_B$/Fe) for bulk Fe.

D. Charge state of Fe

CEMS allows one to identify different site occupations, charge and magnetic states of $^{57}$Fe. The hyperfine parameters calculated according to the evaluations of the spectra are given in Table II. All isomer shifts are given relative to an $\alpha$-Fe reference foil. In general, the implanted Fe occupy three different states: metallic Fe, Fe$^{2+}$ and Fe$^{3+}$ ions dispersed in the ZnO matrix and finally Fe$^{3+}$ in Zn-ferrites. The hyperfine interaction parameters obtained from the best fits are different from that of ferromagnetic $\alpha$ or γ-Fe$_2$O$_3$ or ferrimagnetic Fe$_3$O$_4$. Hence, the presence of these phases was excluded. The dispersed ionic Fe could substitute onto Zn site.

Figure 6(a) and 6(b) show the comparison of Fe implanted ZnO at 623 K with a fluence of $0.4 \times 10^{16}$ and $4 \times 10^{16}$ cm$^{-2}$, respectively. In spectrum (a), the singlet S and doublet D(I) are attributed to Fe$^{3+}$, while the doublet D(II) is from Fe$^{2+}$. In the high fluence sample (spectrum (b)), the majority of Fe are ionic states Fe$^{3+}$ (singlet S) and Fe$^{2+}$ (doublet D(I) and D(II)), while a considerable fraction of a sextet associated to $\alpha$-Fe is present (sextet M). The formation of $\alpha$-Fe is in agreement with SR-XRD observation (Figure 4). At room temperature, all Fe$^{2+}$ and Fe$^{3+}$ show no ferromagnetic interaction. Later on in subsection III we show that even at 5 K the measured ferromagnetism can only be attributed to $\alpha$-Fe NCs.
### TABLE III: Hyperfine parameters obtained from the evaluation of CEMS for samples implanted or annealed at different temperatures. The fluence was \(0.4 \times 10^{16}\) cm\(^{-2}\) for the first sample, while \(4 \times 10^{16}\) cm\(^{-2}\) for all other samples. The codes of S1, S2 and S3 notate the samples for post-annealing process. The notations for the fitting lines are given as S (singlet), D (doublet) and M (sextet).

| Code | \(T_{\text{imp.}}\) (K) | \(T_{\text{ann.}}\) (K) | Fraction \(a\) (%) | IS \(b\) (mm/s) | FR \(a\) (%) | IS \(b\) (mm/s) | QS \(c\) (mm/s) | Fraction \(a\) (%) | IS \(b\) (mm/s) | QS \(c\) (mm/s) | B\(_{hf}\) \(d\) (T) | M (α-Fe) |
|------|-----------------|-----------------|----------------|-------------|----------|-------------|-------------|----------------|-------------|-------------|------------|-----------|
| S1   | 623             | -               | 27.7          | 0.57        | 13.7     | 0.31        | 0.75        | 58.6          | 0.81        | 0.79        | -          | -         |
| S1   | 623             | 823             | 32.8          | 0.53        | 31.5     | 0.78        | 1.29        | 23.2          | 0.96        | 0.58        | 12.5       | 0.06      |
| S1   | 623             | 1073            | 42.6          | 0.42        | 16.7     | 0.68        | 1.52        | 22.5          | 0.94        | 0.54        | 18.2       | 0.07      |
| S2   | 253             | -               | 13.6          | 0.22        | 14.1     | 0.24        | 0.65        | 72.3          | 0.92        | 0.97        | -          | -         |
| S2   | 473             | -               | 22.2          | 0.32        | 9.7      | 0.27        | 0.63        | 68.1          | 0.94        | 0.77        | -          | -         |
| S2   | 253             | 823             | 6.2           | -0.09       | 46.8     | 0.42        | 0.39        | 18.2          | 0.88        | 0.51        | 28.8       | 0.04      |
| S3\(f\) | 623            | -               | 23.0          | -0.09       | 26.3     | 0.45        | 0.32        | 37.3          | 0.91        | 0.80        | 13.4       | 0         |
| S3   | 623             | 823             | 13.9          | -0.09       | 31.4     | 0.45        | 0.35        | 15.9          | 0.92        | 0.58        | 38.8       | 0.02      |

\(a\) Fraction corresponding to the relative area of the subspectrum.

\(b\) Isomer shift: 0 mm/s for α-Fe, 0.7-1.2 mm/s for Fe\(^{2+}\), 0.2-0.7 mm/s for Fe\(^{3+}\), and -0.1 mm/s for γ-Fe.

\(c\) Quadrupole splitting.

\(d\) Magnetic hyperfine field.

\(e\) Hyperfine field distribution.

\(f\) ZnO epitaxial thin films.

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**Figure 6:** Room temperature CEMS for ZnO bulk crystals implanted with \(^{57}\)Fe with different fluences, and with post-annealing. The notations for the fitting lines are given as S (singlet), D (doublet) and M (sextet). The fluence and the process temperatures are indicated.

2. **Implantation temperature dependence**

Figure 7(a) and 7(b) shows CEMS for the samples implanted at low temperatures, 473 K and 253 K, respectively, with a \(^{57}\)Fe fluence of \(4 \times 10^{16}\) cm\(^{-2}\). In these two samples, ionic Fe are the dominant charge states: Fe\(^{3+}\) (S and D(I)), and Fe\(^{2+}\) (D(II)). In contrast to Figure 6(b), there is no detectable α-Fe in these two samples. This is also in agreement with SR-XRD results (Figure 5), where up to an implantation temperature of 473 K no α-Fe is found.

E. **Implantation Energy dependence**

1. **Evolution with post-annealing**

The post-annealing was performed on selected samples: S1 and S2 (Table III). They were implanted with the same fluence of \(4 \times 10^{16}\) cm\(^{-2}\) at 623 K and 253 K, respectively. For sample S1, upon annealing at 823 K for 15 min, the intensity of the sextet increases up to 18.2% while the fraction of Fe\(^{3+}\) (doublet D(I)) decreases, suggesting the growth of the α-Fe nanoparticles and the recovery of lattice defects (Figure 6(c)). Moreover, the value for the magnetic hyperfine field \(B_{hf}\) increases upon annealing and moves closer (from 30.5 T to 31.7 T) to the known value for bulk α-Fe (33 T). For sample S2, after annealing at 823 K for 15 min, the relative fraction of metallic α-Fe increases up to 28.8%. The hyperfine field
FIG. 7: Room temperature CEMS for ZnO implanted with 57Fe at 253 K and subsequent annealed at 823 K for 15 min. The notations for the fitting lines are given as S (singlet), D (doublet) and M (sextet). On the right side of the spectra, the probability distribution P for the magnetic hyperfine field \(B_{hf}\) (solid lines) are given.

is distributed with maxima at 18 T, 27 T and mostly at 32.5 T (\(\alpha\)-Fe). Comparing with the annealing of sample S1, a larger fraction of \(\alpha\)-Fe is formed in the annealed sample S2. This is consistent with a larger magnetization measured by SQUID (shown later). In addition, a small fraction of singlet (S) presents, which is attributed to \(\gamma\)-Fe according to the isomer shift.

Higher temperature (1073 K) annealing was performed on sample S1 and has been reported in Ref [27]. After annealing at 1073 K for 3.5 hours, Fe\(^{3+}\) is the only charge state, and Zn-ferrites (ZnFe\(_2\)O\(_4\)) are formed and are crystallographically oriented inside ZnO matrix.

**F. Magnetic properties Fe implanted ZnO**

In the previous sections, we have reported a thorough investigation on the structural properties, and the charge states of Fe. The main conclusion can be summarized as follows (i) upon implantation at a temperature of 623 K, a small part (around 12%) of the implanted Fe ions forms as crystalline Fe already in the as-implanted state, while the major part of the implanted Fe is in ionic states (Fe\(^{2+}\), and Fe\(^{3+}\)); (ii) implantation at a low temperature (253 K) suppresses the metallic Fe formation, and the implanted Fe ions are in ionic states, but they are not magnetically coupled at room temperature; (iii) post-annealing at 823 K largely enhances the Fe NC formation in all implanted samples for both implantation temperatures (253 K and 623 K). Since CEMS was performed at room temperature only, the magnetic properties of metallic and ionic Fe at low temperature could not be determined. Here we present the results from SQUID magnetometry measured from 5 K to 350 K. We will show that the metallic Fe NCs are superparamagnetic, and they are the predominant contribution to the measured ferromagnetic response even at 5 K. In contrast, the ionic Fe is not ferromagnetically coupled even at 5 K.

1. **Superparamagnetism of Fe NCs**

For magnetic nanoparticles, the formation of domain walls is energetically unfavorable and below a certain size (typically in the range of 15 to 30 nm depending on the material), the particle stays in a single-domain configuration. The magnetism of a single nanoparticle in a solid matrix can be described by the Néel process [57]. If the particle size is sufficiently small, above a particular temperature (so-called blocking temperature, \(T_B\)) thermal fluctuations dominate and no preferred magnetization direction can be defined. Such a system of superparamagnetic particles does not exhibit a hysteresis loop above \(T_B\); therefore the coercivity (\(H_C\)) and the remanence (\(M_R\)) are both zero. Phenomenologically there are two characteristic features in the temperature dependent magnetization of a nanoparticle system. One is the irreversibility of the magnetization in a small applied field (e.g. 50 Oe) after zero field cooling and field cooling (ZFC/FC) [57]. The other is the drastic drop of the coercivity and of the remanence at a temperature close to or above \(T_B\) [58].

For a dc magnetization measurement in a small magnetic field by SQUID, the blocking temperature \(T_B\) is given by

\[
T_B \approx \frac{K_{eff}V}{30k_B}
\]

where \(K_{eff}(V)\) is the anisotropy energy density, \(V\) the particle volume, and \(k_B\) the Boltzmann constant [57]. With this equation, one can estimate the particle size [58]. However, in any fine particle system, there is a distribution of particle sizes, which is usually assumed as a log-normal distribution \(D(V)\).

\[
D(V) = \frac{A}{\sqrt{2\pi}\sigma_L V} \exp\left[-\frac{\ln(V/V_{mean})^2}{2\sigma_L^2}\right]
\]

where \(V_{mean}\) is the most probable value, and \(\sigma_L\) is the standard deviation.

Such a volume distribution results in a distribution of blocking temperatures \(T_B(V)\). The ZFC magnetization can be calculated as follows [57].
\[ M_{ZFC}(B,T) = \frac{M_s^2(T)B}{3k_BT} \frac{1}{N} \int_{V_{limit}(T)}^{V^2 D(V)dV} + \frac{M_s^2(T)B}{3K_{eff}} \frac{1}{N} \int_{V_{limit}(T)}^{\infty} V D(V)dV \] (4)

where \( M_s \) is the spontaneous magnetization of the particle, \( D(V) \) the volume distribution, \( V_{limit}(T) = \frac{30k_BT}{K_{eff}} \) the maximum volume in the superparamagnetic state, \( N \) the normalizing factor, and \( k_B \) the Boltzmann constant. \( M_s \) is assumed to be a constant independent of temperature \([57][59]\). The first integral represents the contribution of the superparamagnetic particles, while the second corresponds to the blocked ones. A more precise determination of the size should be performed by fitting the ZFC curve with the equation 4. Figure 8 shows the fitting on the ZFC magnetization curve, and the corresponding size distribution. In the fit, \( K_{eff}(V)=5\times10^4 \text{ J m}^{-3} \) is treated as a constant.

2. Fluence dependence

Figure 9(a) shows the ZFC/FC magnetization curves in a 50 Oe field for different fluences of Fe implanted ZnO. The FC curves for low fluences of 0.1×10^{16} (not shown for clarity) and 0.8×10^{16} cm\(^{-2}\) completely overlap with the corresponding ZFC curves at values close to zero. No superparamagnetic particles are present in the two samples. For larger fluences (above 2×10^{16} cm\(^{-2}\)), a distinct difference in ZFC/FC curves was observed. ZFC curves show a gradual increase (deblocking) at low temperatures, and reach a broad peak with a maximum, while FC curves continue to increase with decreasing temperature. The broad peak in the ZFC curves is due to the size distribution of Fe NCs. In this paper, the temperature at the maximum of the ZFC curve is taken as the average blocking temperature (later referred as \( T_B \)). At a much higher temperature than \( T_B \), FC curves still depart from corresponding ZFC curves, which distinguish the Fe particle system from a conventional spin-glass system where the FC curve merges together with ZFC curve just at \( T_B \) and shows a plateau below \( T_B \) \([60]\). The ZFC/FC curves are general characteristics of magnetic nanoparticle systems with a broad size distribution \([61]\). \( T_B \) increases with the fluence, i.e. the size of nanoparticles. Table II lists the average size of Fe NCs calculated by Eq. 2 and by XRD data (Eq. 1), and simulated by Eq.
Figure 10 shows the magnetization versus field reversal (M-H) of samples implanted with large fluences. At 5 K, hysteretic behaviors were observed for all three samples. The saturation moment is increased with increasing fluence, however the coercivity is decreased from 600 Oe for a fluence of $2 \times 10^{16}$ cm$^{-2}$ to 330 Oe for larger fluences (see table I). This can be explained by the enhanced coercivity effect for the interfacial spins, which increases with decreasing the size of nanoparticles [63]. The inset shows the M-H curve at 300 K for the sample implanted with the fluence of $4 \times 10^{16}$ cm$^{-2}$. As expected for a magnetic nanoparticle system, above the blocking temperature, both remanence and coercivity drop to zero.

3. Implantation temperature dependence

Figure 10(b) shows the magnetization versus field reversal of samples implanted with Fe ($4 \times 10^{16}$ cm$^{-2}$) at different implantation temperatures. Only the sample implanted at 623 K shows a hysteretic behavior due to the presence of Fe NCs, while the other samples implanted at 473 K or below show no ferromagnetic response down to 5 K. This is in full agreement with SR-XRD and CEMS measurements.

4. Post annealing effect

The magnetic properties of the samples implanted at 623 K have been reported in a previous paper [27]. The main conclusions are the following: the annealing at 823 K results in the growth of $\alpha$-Fe NCs. During annealing at 1073 K the majority of the metallic Fe is oxidized; after a long term annealing at 1073 K, crystallographically oriented ZnFe$_2$O$_4$ NCs form. Here we mainly present the annealing at 823 K for the samples implanted at 253 K. Due to the different initial state from the 623 K implanted samples, the same annealing temperature leads to different results.

Figure 11 shows the magnetic properties of the samples implanted at 253 K with subsequent post annealing. In the as-implanted state, there is no ferromagnetism down to 5 K, while after 823 K annealing, magnetization of $0.52 m_B/Fe$ was observed. The ZFC/FC magnetization curves show the characteristics of magnetic nanoparticle system. According to SR-XRD and CEMS results, we attribute this to Fe NCs. The ZFC curve is very broad and $T_B$ is above room temperature. The M-H curves at 300 K for both cases are still open, although with much smaller coercivity and remanence compared with 5 K. However the magnetic properties are quite different from the 623 K implanted sample after post annealing at 823 K, where the $T_B$ is well below 300 K, and at 300 K there is neither coercivity nor remanence. We will discuss this difference in section IV.
FIG. 11: Hysteresis loops measured at 5 K for ZnO implanted with 180 keV Fe at 253 K (as-implanted and post annealed). The fluence is $4 \times 10^{16}$ cm$^{-2}$. For comparison, the sample implanted with the same energy and fluence, but at a high implantation temperature (623 K), after the same annealing process is shown as the solid line. (b) ZFC/FC magnetization of the sample after 823 K annealing. The arrows indicate the blocking temperatures.

5. Magnetic anisotropy of Fe NCs

M-H loops were also measured for selective samples which have been implanted with a fluence of $4 \times 10^{16}$ cm$^{-2}$ with the field applied perpendicular to the sample surface. Figure 12 shows the comparison of the magnetization between the in-plane and out-of-plane direction at 5 K. The in-plane (parallel to the ZnO surface) is the easy axis, while the out-of-plane (perpendicular) is the hard axis. At 5 K, the coercivity of the easy axis is around 360 Oe, and the ratio of $M_R/M_S$ (remanence and saturation moment) is around 58%. The anisotropy energy, $K$, can be calculated according to the equation of $K = M_A H_A/2$, where $M_s$ is the saturation moment of $4\pi M_s = 22000$ G, $H_A$ is the effective anisotropy field. Indeed $H_A$ is rather difficult to be deduced since it is not easy to measure a real hard axis loop with SQUID magnetometry without a precise control of the sample alignment. Moreover the size distribution of Fe NCs could result in a distribution of $H_A$. Therefore, we deduce a lower and upper limit of $H_A$ according to the shape of the hard axis loop. Using this approach, the anisotropy energy is estimated to be in the range of $(1.8-3.3) \times 10^5$ Jm$^{-3}$. It is larger than the magnetocrystalline anisotropy, and around one order of magnitude larger than the uniaxial anisotropy observed in Fe thin films [64] and micro-scale Fe nanomagnets [65]. If the Fe NCs are assumed to be sphere-like, their magnetism should be isotropic, unless they are textured. However as found by XRD, these Fe NCs are not textured. This magnetic anisotropy could be due to the shape effect of Fe NCs, i.e. they are not sphere-like, or magnetostriction. There is, however, no evidence for any of these two possibilities.

FIG. 12: Hysteresis loops measured at 5 K for Fe implanted ZnO at 180 keV and 623 K up to a fluence of $4 \times 10^{16}$ cm$^{-2}$. The field is changed from parallel to perpendicular with respect to the sample surface, revealing the magnetic anisotropy. The intersections between the easy axis M-H curve and solid and dashed direct lines indicate the lowest and highest $H_A$.

6. Memory effect of Fe NCs

Below the blocking temperature, a magnetic nanoparticle system has a rich and unusual behavior. For instance a slow relaxation and a history-dependent magnetic memory are found in the dc magnetization as a function of temperature [60][61][66][67][68]. In our system, Fe nanoparticles embedded inside ZnO crystals, the temperature dependent memory effect was also observed (Figure 13) using a cooling and heating protocol suggested by Sun et al. [64]. At 300 K a magnetic field of 50 Oe was applied and the sample was cooled down to 5 K at a constant cooling rate of 3 K/min. Then the sample was heated continuously at the same rate and the magnetiza-
FIG. 13: Temperature dependent memory effect in the dc magnetization. The reference curve is measured on heating at a constant rate of 3 K/min after FC in 50 Oe. The solid squares are measured during cooling in 50 Oe at the same rate but with a stop of 2 hours at 50 K. The field is cut off during stop. The open circles are measured with continuous heating at the same rate after the previous cooling protocol. Inset shows the reciprocal magnetization versus temperature.

The obtained M(T) curve is referred as the reference curve (solid line in Figure 13). Thereafter, we cooled the sample at the same rate and recorded the magnetization with cooling, but temporarily stopped at T = 50 K for a waiting time of 2 hours. During waiting time, the field was switched off. After the stop, the 50 Oe field was reapplied and cooling and measuring were resumed. The temporary stop resulted in a steplike M(T) curve (solid squares in Figure 13). After reaching the lowest temperature 5 K, the sample was heated back with the rate of 3K/min in the same field, and the magnetization was recorded again. The M(T) curve during this heating also has a steplike behavior at the stop temperature of 50 K, then recovers the previous M(T) curve measured during cooling. The system remembers its thermal history.

Two explanations have been suggested for such a memory effect [67]. The first one is a broad distribution of blocking temperatures originating from the distribution of the anisotropy energy barriers. Another explanation is the strong dipolar interaction between nanoparticles, which frustrates the nanomagnetic moments, and slows down their relaxation. Our observations rather support the first model. First of all, the memory effect is also observed for two other samples ($2 \times 10^{16}$, and $8 \times 10^{16}$ cm$^{-2}$) (not shown). Therefore the effect is independent of ion fluence, i.e. particle density. Second, the inset of Figure 13 shows the reciprocal FC magnetization at 500 Oe versus temperature. The perfect linearity of the curve for T>50 K strongly suggests that the dynamics of the nanoparticles above blocking temperature can be well described by superparamagnetism. Therefore, the magnetic properties of the sample depend only on the individual particle behavior. Third, the size of Fe nanoparticles is widely dispersed according to the analysis on the ZFC magnetization curve as shown in Figure 8. Therefore, we would attribute the memory effect to the broad distribution of particle size, i.e. of anisotropy energy barriers.

G. Fe implanted epitaxial ZnO layers

The epitaxial ZnO layers used in this study were grown by pulsed layer deposition on Al$_2$O$_3$(0001). These thin films are n-type conducting with a carrier concentration of $10^{15}$-$10^{17}$ cm$^{-3}$ at room temperature. Details about the sample preparation can be found in Refs. [69][70][71]. $^{57}$Fe ions were implanted at an energy of 180 keV at 623 K. Then the samples were subjected to the same thermal annealing, and structural as well as magnetic characterization like the bulk crystals.

1. Formation of Fe NCs

Figure 14 shows the XRD 2θ-θ scans of Fe implanted ZnO epitaxial layers (as-implanted and post annealed at 823 K). In the left panel, one can see the nice epitaxy of ZnO on Al$_2$O$_3$(0001) with the out-of-plane relationship of ZnO(0001)∥Al$_2$O$_3$(0001). The right panel is a zoom on the Fe-related peak region. A single crystal sample implanted with the same fluence and at the same temperature is shown for comparison. Obviously, the epitaxial ZnO behaves differently from the bulk crystals upon Fe implantation. In the epitaxial-layer, γ-Fe is the predominant phase, while it is α-Fe in the single crystal. This difference will be discussed in section IV. Upon thermal annealing at 823 K, the epitaxial ZnO behaves similar to the low temperature implanted bulk crystals. Both metallic Fe phases (α and γ) are growing.
FIG. 15: Room temperature CEMS for ZnO epitaxial thin films as-implanted with 57Fe and post-annealed at 823 K for 15 min. The notations for the fitting lines are given as S (singlet), D (doublet) and M (sextet). On the right side of the spectra, the probability distribution P for the magnetic hyperfine field (B_{hf}, solid lines) are given.

2. Charge state of Fe

The charge and chemical states of Fe deduced from CEMS are shown in Figure 15. The hyperfine interaction parameters are given in Table III. In the as-implanted sample, ionic Fe is the predominant phase, while also α- and γ-Fe are present (sextet M and singlet S, respectively). After annealing at 823 K, the fraction of ferromagnetic α-Fe is drastically increased from 13.4% to 38.8%. In the bulk crystal implanted at the same condition, there is no γ-Fe neither in as-implanted nor in annealed samples. Also the fraction of α-Fe after annealing (18.2%) is much lower than that in epitaxial films (38.8%).

3. Magnetic properties

The ZFC/FC magnetization measurements for the as-implanted and 823 K annealed samples (Figure 16(a)) shows the typical behavior of a magnetic nanoparticle system. However T_B in the ZFC curves increases from 26 K to around 300 K with post annealing. The absolute magnetization value per Fe in the ZFC/FC curves for the annealed sample is lower than that of the as-implanted sample. This is due to the fact that there are more bigger Fe NCs after annealing, and the bigger NCs are more difficult to be aligned at such a small field of 50 Oe. Figure 16(b) shows the M-H curves. The coercivity is not significantly changed with annealing, while the saturation magnetization is increased from 0.55\mu_B/Fe to 1.3\mu_B/Fe at 5 K and from 0.24\mu_B/Fe to 1.1\mu_B/Fe at 300 K, respectively, with annealing. For both samples, the M-H loops show no hysteresis at 300 K without coercivity and remanence. Obviously, the annealing behavior is different from the single crystal implanted at same temperature of 623 K, but similar to the single crystal implanted at 253 K. We will discuss this point in section IV.

IV. DISCUSSIONS

A. Phase diagram of Fe in ZnO

In section III we present the structure and magnetic properties of Fe implanted ZnO. The implantation parameters, i.e. fluence, energy, temperature, were varied. In general, metallic Fe NCs have been formed already in the as-implanted state when the implantation temperature is above 623 K and the fluence is above 2 \times 10^{16} \text{cm}^{-2}. By summarizing all results, a phase diagram of
Fe in ZnO can be sketched, as shown in Figure 17. Note that the materials studied in this research are ZnO bulk crystals grown by hydro-thermal method. They are semi-insulating in the as-purchased state with n-type carrier concentration of $10^{12}$-$10^{14}$ cm$^{-3}$. The phase diagram will likely be different for epitaxial-ZnO and for p-type ZnO.

**B. Phase separation depends on the forms of ZnO**

In section III we have shown the structural and magnetic properties of ZnO bulk crystals and epitaxial thin films implanted at the same temperature and with the same Fe fluence. They are obviously different from each other (see table I). In the bulk crystals, only 11% (increased to 15% after 823 K post annealing) of the implanted Fe is ferromagnetic and mainly α-Fe, while 25% in the epitaxial ZnO films (increased to 59% after 823 K post annealing). Recently Dietl proposed the self-organized growth driven by the charge state of the magnetic impurities [45][72]. The energy levels derived from the open d shells of transition metals reside usually in the bandgap of the host semiconductor. The mid-gap levels of magnetic impurities trap carriers origination from residual impurities or defects. This trapping alters the charge state of the magnetic ions and hence affects their mutual Coulomb interactions. Therefore, different carriers (electrons or holes, with different concentrations) could lead to different interactions (e.g. repulsions and attractions) between the implanted transition metal ions, and finally result in a different phase separation. Both ZnO materials (bulk crystals and epitaxial thin films) used in this study are n-type semiconductors. The carrier concentration is around $10^{12}$-$10^{13}$ cm$^{-3}$ for bulk crystals and $10^{15}$-$10^{17}$ cm$^{-3}$ for epitaxial thin films [69][70] at room temperature. Therefore, we can explain the different behavior in ZnO bulk crystals and epitaxial layers upon Fe implantation in the above-mentioned model. A higher concentration of free electrons leads to more agglomerations of Fe. Moreover the nanocrystal aggregation could be largely reduced or avoided by the realization of p-type doping in ZnO.

However, one has to note that there are a lot of defects, such as dislocations, and stacking faults, in the epitaxial ZnO films grown on Al$_2$O$_3$ due to the large lattice mismatch [73]. Kaiser *et al.* demonstrated that in high fluence Er implanted SiC, the defects act as nucleation sites in the formation of Er-atom clusters and NCs [74]. A similar effect can be present in the case of Fe implanted ZnO films.

**C. Annealing behavior depends on the initial state**

Note that three kind of samples have been annealed at the same temperature of 823 K. One is the ZnO single crystal implanted at 623 K, in which Fe NCs have already been formed in the as-implanted states. One is the ZnO single crystal implanted at 253 K, in which no Fe NCs could be detected in the as-implanted sample. The last one is the ZnO thin film implanted at 623 K, in which rather small Fe NCs have been formed in the as-implanted sample compared to that in the single crystal. The annealing behavior in the first case is quite different from the later two cases. One reason is the fact that diffusion of Fe NCs is much more difficult than of single Fe ions. In the 623 K implanted sample, Fe NCs have already been formed, and they are not so mobile during 823 K annealing. Therefore the size and the amount of Fe NCs only slight increase after annealing. However, in the sample without Fe NCs or with very small NCs, Fe ions are more mobile with annealing, and they aggregate into rather larger Fe NCs. Another reason could be the same as discussed in the above section, given the fact that implantation at 253 K induces more point defects than that 623 K (see Figure 2).

**D. Magnetic coupling of dispersed ionic Fe**

Although a part of the implanted Fe ions aggregated to metallic NCs, the remaining are in the ionic state. Even after 823 K annealing, there is still a considerable amount of ionic Fe. By SR-XRD no crystalline Fe-oxides could be detected. Therefore, these ionic Fe could be diluted inside ZnO matrix. Moreover, Ref. [51] demonstrated that the implantation-induced electrical isolation of ZnO is removed after annealing between 773 to 873 K. Therefore, the carrier concentration is comparable with the virgin sample after annealing at 823 K. However, as measured by SQUID down to 5 K and CEMS at room temperature, Fe$^{2+}$ and Fe$^{3+}$ are not ferromagnetically coupled.
In addition to conventional thermal annealing which is an equilibrium process, a nonequilibrium annealing technique, i.e., flash lamp annealing at a pulse length of 20 ms, was also used by us \[72\]. For an intermediate light power, the implantation-induced surface defects could be removed without creation of secondary phases within the implanted region. However, there is still no detectable ferromagnetic coupling between these dispersed Fe ions.

Moreover, currently the absence of ferromagnetism in transition metal doped ZnO is a universal problem. Several groups have shown that transition metal ions, e.g., Fe\[70\], Mn \[17\], and Co \[17\], are substitutional inside ZnO. However, no ferromagnetism could be observed due to the possible reason of the lack of p-type conductivity.

V. SUMMARY AND CONCLUSIONS

(1) In general, a combination of SR-XRD, ZFC/FC magnetization and element specific spectroscopy measurements is a reliable approach to clarify the observed magnetism in DMS materials.

(2) By correlating the structural and magnetic properties of all investigated samples, it is clear that ferromagnetism is only observed when $\alpha$-Fe (or ZnFe$_2$O$_4$) NCs are present. In as-implanted and 823 K annealed samples, dispersed Fe$^{2+}$ and Fe$^{3+}$ are the predominant charge states. However, they are not ferromagnetically coupled.

(3) $\alpha$-Fe (bcc) NCs are not crystallographically oriented inside ZnO matrix. However, fcc-ZnFe$_2$O$_4$ NCs formed after annealing at 1073 K are epitaxially embedded in ZnO. This is due to the crystalline symmetry. Hexagonal ZnO crystals are six-fold symmetric, while $\alpha$-Fe is four-fold symmetric. Fcc-ZnFe$_2$O$_4$ is also six-fold symmetric viewed along [111] direction.

(4) The magnetic properties of these Fe NCs were carefully investigated regarding their memory effect and magnetic anisotropy. A memory effect is observed in the temperature dependent magnetization measurement, which is induced by the different relaxation times originating from the different grain sizes of the Fe nanoparticles, and consequently different anisotropy energy barriers. The in-plane magnetic anisotropy could be due to the shape effect.

(5) The phase separation, i.e., the formation of metallic Fe, depends on the initial state of the host materials, namely the carrier and/or the defect concentrations. The n-type carriers could facilitate the self-organization of metallic Fe NCs.

(6) The next question is directed to the magnetically activated dilution of metallic ZnO. The realization of p-type doping for ZnO could be the solution.

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