Hyperfine Interact
DOI 10.1007/s10751-011-0403-8

# A CEMS search for precipitate formation in $^{57}$Fe implanted ZnO

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**Abstract** Conversion electron Mössbauer Spectroscopy measurements have been made on ZnO single crystals implanted with 60 keV $^{57}$Fe to 4 and 8 at.% peak concentrations, and annealed up to 800°C. The spectra show quite strong changes with annealing, but no evidence of magnetic components, thus precluding the formation of large sized precipitates or secondary phases. Above an annealing temperature of 650°C, the dominant spectral component is a doublet with hyperfine parameters typical of $Fe^{3+}$, which is attributed to $Fe^{3+}$ ions in nano-precipitates ~5 nm in size.

**Keywords** ZnO · $^{57}$Fe implanted · CEMS · Nano-precipitates

## 1 Introduction

The theoretical work of Dietl et al. [1] and Sato and Katayama-Yoshida [2], predicting room temperature ferromagnetism (RTFM) in p-type ZnO implanted with ≥5% Mn ions as well as other transition metal (TM) ions, spawned a flurry of experimental investigations on the search for RTFM in transition metal doped ZnO and other

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Published online: 08 November 2011

metallic oxides. The experimental results however have been ambiguous and often contradictory regarding the magnetic properties of different $Zn_{1-x}TM_xO$ systems, and revisit of earlier measurements [3] and reviews [4, 5] have questioned whether the TM ions are uniformly distributed in the host matrix on the appropriate atom site or if clusters, precipitates or secondary phases are responsible for the observed magnetic effects.

An understanding of the behaviour of the incorporated TM atoms and their impact on the crystal structure of the host is essential if the desired magnetic properties are to be realised. In a recent study Schumm et al. [6] applied Raman scattering and XRD measurements to study impurity incorporation, induced defects and disorder in ZnO implanted with TM ions with a step-like profile with concentrations up to 16 at.%. Their results showed the presence of micro-precipitates, and additionally secondary phases in samples with ≥8 at. % Mn ions.

In this contribution we present results of our conversion electron Mössbauer spectroscopy (CEMS) investigations on ZnO implanted with $^{57}Fe$ ions with 60 keV energy and to peak concentrations of 4 at.% and 8 at.%.

## 2 Experimental details

Mass separated $^{57}Fe$ ions were implanted with 60 keV energy at room temperature into ZnO single crystal substrates commercially available from Crystec GmbH, Berlin. TRIM simulations gave a Gaussian implantation profile with a mean depth of about 30 nm and half-width (HWHM) of about 10 nm. The implantation fluence was chosen to give $^{57}Fe$ peak concentrations of 4 and 8 at.%. CEMS measurements were made at room temperature, on the as-implanted samples and after annealing the samples for 30 min in flowing $N_2$ at temperatures up to 800°C.

## 3 Results and discussion

Figure 1 presents the CEMS spectra of ZnO single crystals implanted with $^{57}Fe$ to peak concentrations of (a) 4 at.% (ZnO:Fe4) and (b) 8 at.% (ZnO:Fe8), respectively (corresponding to respective fluencies of $1.2 \times 10^{16}$ $^{57}Fe/cm^2$ and $2.4 \times 10^{16}$ $^{57}Fe/cm^2$), and annealed at the temperatures indicated. The set of spectra for each sample was analyzed in a simultaneous fit to the data obtained after the annealing at the different temperatures. The fit components and their assignments are listed in Table 1, where isomer shifts are given relative to $\alpha$-Fe.

On implantation, the spectra of both samples show significant contributions (>50%) from Fe in defect sites in the ZnO lattice ($Fe_D$) plus an asymmetric doublet with isomer shift and quadrupole splitting consistent with $Fe^{2+}$ on substitutional Zn sites in the wurtzite lattice. The spectra show dramatic changes with annealing, but no evidence of any magnetic component, thus ruling out the formation of large sized precipitates or secondary (ZnFeO) complexes.

After the annealing at 350°C, the $Fe_D$ fraction reduces to 6% and 12%, respectively, for ZnO:Fe4 and ZnO:Fe8, and a second doublet with hyperfine parameters of $Fe^{3+}$ appears. After annealing at $T_A \geq 650$°C, the spectra of both samples are dominated by a quadrupole doublet which accounts for >80% of the spectral area

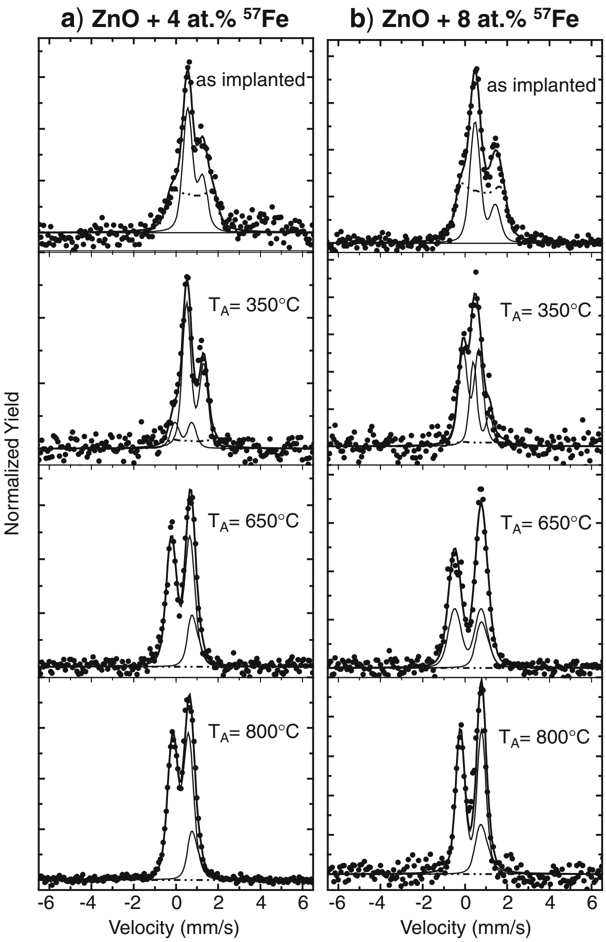


**Fig. 1** CEMS spectra of ZnO single crystals implanted with **a**) 4 at.% and **b**) 8 at.% $^{57}$Fe, observed after annealing at the temperatures indicated

at $T_A = 800°C$. The isomer shift and quadrupole splitting ($\Delta E_Q$) of the doublet for ZnO:Fe4 (ZnO:Fe8) have values of 0.28 (0.22) mm/s and 1.00 (0.75) mm/s, which are typical of parameters for $Fe^{3+}$, but larger than the values for substitutional $Fe^{3+}$ in ZnO [7]. As stated above, Schumm et al. [6] conducted Raman scattering and XRD measurements on ZnO samples implanted with TM ions at a range of energies to give a step-like profile with concentrations up to 16 at.% (total implantation fluencies up to $2.5 \times 10^{17}/cm^2$). Their results showed the presence of micro-precipitates, and additionally secondary phases in samples with ≥8 at.% Mn ions. In the present measurements the peak implantation fluence is an order of magnitude lower, and the absence of secondary phases is not unexpected. However, [6] also shows the presence of micro-precipitates even in the samples with lower TM ion concentrations. We therefore attribute the dominant doublet observed at $T_A \geq 650°C$ to nano-sized $Fe^{3+}$ precipitates, the absence of any magnetic components in the spectra indicating that these are ~5 nm in size.

**Table 1** Hyperfine parameters (isomer shift $\delta$, quadrupole splitting $\Delta E_Q$) and Gaussian broadening $\sigma$ of the components required to fit the spectra presented in Fig. 1

| $T_A$ | | ZnO:Fe4 | | | ZnO:Fe8 | | |
|---|---|---|---|---|---|---|---|
| | | $\delta$ (mm/s) | $\Delta E_Q$ (mm/s) | $\sigma$ (mm/s) | $\delta$ (mm/s) | $\Delta E_Q$ (mm/s) | $\sigma$ (mm/s) |
| As-implanted | $Fe^{2+}$ | 0.96(2) | −0.97(2) | 0.19 | 0.91(2) | −0.71(2) | 0.18 |
| | $Fe_D$ | 0.74(2) | 1.33(3) | 0.10 | 0.74(2) | 1.33(2) | 0.10 |
| 350°C | $Fe^{2+}$ | 0.78(2) | −0.77(2) | 0.12 | 0.91(2) | −0.81(2) | 0.15 |
| | $Fe_D$ | 0.74(4) | 1.33(4) | 0.10 | 0.74(4) | 1.33(4) | 0.10 |
| | $Fe^{3+}$ | 0.28(2) | 0.75(2) | 0.18 | 0.35(2) | 0.80(2) | 0.17 |
| 650°C | $Fe^{2+}$ | 0.92(2) | −0.37(2) | 0.19 | 0.91(2) | −0.35(2) | 0.15 |
| | $Fe^{3+}$ | 0.14(2) | 1.25(2) | 0.26 | 0.22(2) | 0.87(2) | 0.20 |
| 800°C | $Fe^{2+}$ | 0.90(2) | −0.37(2) | 0.19 | 0.91(2) | −0.35(2) | 0.15 |
| | $Fe^{3+}$ | 0.28(2) | 1.00(2) | 0.17 | 0.22(2) | 0.75(2) | 0.20 |

## 4 Conclusions

We have conducted CEMS measurements on ZnO samples implanted with 4 and 8 at.% $^{57}Fe$.

The spectra show quite dramatic changes with annealing, but no evidence of magnetic components. Above an annealing temperature of 650°C, the dominant spectral component is a doublet with hyperfine parameters typical of $Fe^{3+}$, which is attributed to $Fe^{3+}$ ions in nanoclusters ~5 nm in size.

**Acknowledgement** This study was undertaken within the National Research Foundation (South Africa)—Deutsche Forschungsgemeinschaft (Germany) (contract Ro1198/13-1) bi-lateral research program.

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