Structural impact of Mn implantation on ZnO

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Abstract. We present a systematic analysis of the structural properties of Mn implanted ZnO by Raman scattering and complementary methods in the Mn composition range 0.2–8 at.% (relative to Zn) with an implantation step profile of about 300 nm depth. Mn ions are substitutionally incorporated on Zn sites in the ZnO wurtzite lattice and no secondary phases are detected. Beside the common eigenmodes of the ZnO host lattice, we observe additional modes related to the Mn implantation, which are studied for different Mn concentrations and annealing procedures. We distinguish between implantation damage and impurity induced disorder, and also show that the spectral feature which is often assigned to a Mn local vibrational mode (LVM) in ZnO consists of two separate modes. We present evidence that only one of these features is a candidate for a LVM.

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1. Introduction

In diluted magnetic semiconductors (DMS), nonmagnetic host ions are partially substituted by magnetic ions. Stable ferromagnetic configurations arising from carrier-mediated exchange interaction have been predicted for DMS obtained by alloying ZnO with transition metal (TM) ions, typically in a concentration range of 1–25 at.% relative to the total number of Zn atoms [1, 2]. Since the prediction of room temperature ferromagnetism for (p-type) Zn$_{1-x}$Mn$_x$O [1], the interest in this DMS is huge because of its possible use for future spintronics applications [3].

However, reviews of the experimental situation show ambiguous and often contradictory results regarding the magnetic properties of different Zn$_{1-x}$Mn$_x$O systems [4]. A key question for such DMS systems is whether the material contains uniformly distributed transition-metal ions on the appropriate atom site or if clusters, precipitates or secondary phases are responsible for the observed magnetic properties. So, the understanding of the exact incorporation behaviour of the TM atoms and their impact on the ZnO wurtzite crystal structure is crucial for the desired magnetic properties. To address these questions we applied Raman scattering, as a versatile technique for a fast and non-destructive study of impurity incorporation, induced defects and disorder in the host lattice.

There are numerous reports on Raman spectroscopic studies of Zn$_{1-x}$Mn$_x$O, e.g. [5]–[13], few of them deal with Mn-implanted ZnO [6]–[8]. Most of the Raman peaks reported for Zn$_{1-x}$Mn$_x$O directly reflect the wurtzite lattice vibration modes of pure ZnO, well known from literature [14, 15]. In addition, features not present in the Raman spectra of pure ZnO occur. The origin of these features, such as local vibrational modes (LVMs), disorder induced silent modes, or phonon modes by precipitates, is still controversial. Here, we present systematic micro-Raman measurements from room temperature to 10 K using different excitation wavelengths throughout the visible spectral range. Also, we apply annealing steps to clarify the origin of the observed features and to study the structural impact of the impurity incorporation on the host lattice. Beside Raman spectroscopy, x-ray diffraction (XRD) and transmission electron microscopy (TEM) are applied and the magnetic properties are probed by magneto-optical Kerr effect (MOKE) and electron paramagnetic resonance (EPR).
Table 1. Energies and fluences during the Mn\(^{2+}\) ion implantation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluences (cm(^{-2}))</th>
<th>Total fluence (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>450 keV</td>
<td>300 keV</td>
</tr>
<tr>
<td>0.2 at.% Mn impl. ZnO</td>
<td>1.40 × 10(^{15})</td>
<td>5.25 × 10(^{14})</td>
</tr>
<tr>
<td>0.8 at.% Mn impl. ZnO</td>
<td>5.60 × 10(^{15})</td>
<td>2.10 × 10(^{15})</td>
</tr>
<tr>
<td>2.0 at.% Mn impl. ZnO</td>
<td>1.40 × 10(^{16})</td>
<td>5.25 × 10(^{15})</td>
</tr>
<tr>
<td>8.0 at.% Mn impl. ZnO</td>
<td>5.60 × 10(^{16})</td>
<td>2.10 × 10(^{16})</td>
</tr>
</tbody>
</table>

2. Experimental

Commercially available ZnO single crystals (CrysTec GmbH, Berlin, Germany) were implanted at room temperature with manganese ions yielding Mn concentrations of 0.2, 0.8, 2 and 8 at.% relative to Zn. One reference sample was prepared by the implantation of Co with exactly the same ion energies and fluence as the 8 at.% Mn sample. We chose a set of five different ion energies in order to achieve a box-like implantation profile with a resulting layer thickness of about 300 nm (for energies and fluences see table 1). The implantation profile is displayed in figure 1 and was calculated with the Monte Carlo program package SRIM/TRIM [16]. Post-implantation sample annealing was performed at 700°C in air for 15 min. For the 8 at.% sample, a second annealing step (900°C in air for 15 min) was also applied.

XRD analysis of the obtained samples was conducted with a Siemens D5000 diffractometer (Cu–K\(\alpha\)). Cross-section specimens for TEM analysis of the samples were prepared by a FIB system (Novalab 600, FEI). Here, standard preparation procedures were used, and finally the electron transparent specimens were investigated in a high-resolution TEM Philips system (CM 200-FEG-UT) equipped with electron dispersive x-ray spectroscopy (EDX).

EPR experiments on the 700°C annealed Mn implanted ZnO crystals (0.2–8 at.%) were performed at the X band with 9.5 GHz on a Brucker ESP300 spectrometer with a microwave power of 2 mW. All data were taken at room temperature with the magnetic field applied perpendicular to the crystal c-axis.

The magnetic properties of the samples were also measured by the MOKE at room temperature with a linearly polarized He–Ne laser (632.8 nm) in the longitudinal configuration, which probes the in-plane magnetization with a maximal field of 0.15 T.

In the Raman measurements, the scattered light was analysed by a triple monochromator (Dilor XY, focal length 500 mm) and detected with a liquid-nitrogen cooled CCD-array for part of the room temperature and all low temperature experiments. We used the 457.9, 496.5 and 514.5 nm lines from an Ar-ion laser as excitation source. The micro Raman set-up includes the microscope Olympus BHT. We focused the laser light with an 80× ULWD or a standard 100× objective. For the low temperature micro Raman studies we used a Cryotech continuous flow helium cryostat at 10 K. Additional Raman experiments were performed with a Renishaw Raman system RM 1000 (with Leica Microscope DM LM) at room temperature with the 632.8 nm line of a HeNe laser and the 514.5 nm line of an Ar-ion laser as excitation sources. In these experiments the scattered light was analysed by a single monochromator equipped with a double notch filter system. To focus the laser light we used a 50× objective, the signal was detected by a Peltier cooled CCD array.
Figure 1. Profile of manganese ions implanted in ZnO crystals with a concentration of 8 at.%, (a) calculated using SRIM/TRIM [16] and (b) studied by EDX, from bottom to top: Zn K\textsubscript{\alpha}, O K\textsubscript{\alpha} and Mn K\textsubscript{\alpha} (spectra have been scaled vertically for clarity).

3. Structural and magnetic characterization

XRD measurements show no new diffraction peaks occurring in the Mn implanted samples in comparison to the ZnO reference sample. Hence, within the sensitivity level of our XRD experiments we find that no clusters or other phases than ZnO have been formed upon the Mn implantation process or subsequent annealing. Furthermore, the (0002) diffraction of the ZnO crystal reveals a slight broadening, especially in the 8 at.% Mn sample, but no shift of this diffraction peak is observed. The high implantation flux leads to a high defect density, resulting in a locally distorted lattice and the broadened XRD peak.

The conducted TEM experiments confirm the assumption that no secondary phases have been created during ion implantation and subsequent annealing. Figure 2 shows representative cross-section (a) and high-resolution TEM (b) micrographs of the sample implanted with the highest ion fluence (8 at.%). The images clearly demonstrate the presence of remaining defects, seen by the strong variation of the contrast, but also the intact ZnO crystal lattice. We investigated large areas of the implanted region and did not find any indication of the formation of other new Mn–Zn–O phases. EDX experiments confirm the calculated implantation profile (figure 1). Slight differences in the implantation depth between the theoretical calculation and the experimental results may be due to limited depth calibration accuracy of the EDX set-up. MOKE results reveal only a weak paramagnetic signal at room temperature for the sample implanted with the highest ion fluence.
To get information about the oxidation state and site occupancy of the Mn ions in the ZnO lattice, we conducted EPR measurements. As the number of unpaired electrons is different for different oxidation states, they can be distinguished in the EPR spectra. Figure 3 shows the EPR signal for the 8 at.% Mn implanted ZnO sample. A broad signal (red line in the figure) is superimposed by many narrow lines with a sextet having highest intensity. Similar EPR spectra have already been analysed in detail by Schneider and Sircar in the early sixties [17].

The electronic configuration of the Mn$^{2+}$ ion corresponding to its half-filled d-shell is $3d^5$ with spin $S = 5/2$. The only natural isotope is $^{55}$Mn with nuclear spin $I = 5/2$. The resonance of an isolated Mn$^{2+}$ ion located substitutionally on a Zn site in the hexagonal ZnO crystal is described by the spin Hamiltonian:

$$H = g\beta H S + \frac{1}{6} a (S_x^4 + S_y^4 + S_z^4) + D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] + ASI.$$
So in low concentration (< 0.2 at.%) Mn alloyed ZnO, an isotropic Zeeman interaction, a hyperfine interaction and a fine structure splitting are observed. Already in the EPR spectra of our untreated ZnO crystals, this signature occurs, corresponding to Mn$^{2+}$ ions located on Zn lattice sites. This can be accounted to the fact that the ZnO crystals contain Mn$^{2+}$ ions as residual impurities with a concentration as low as about $10^{17}$ cm$^{-3}$. Their concentration is below the sensitivity limit of the Raman scattering method. For increased Mn concentrations (here, by implantation) an antiferromagnetic dipole–dipole interaction between substitutional Mn$^{2+}$ ions occurs and the fine structure vanishes, which results in a broad, unstructured signal [18]. We observe such a broad background signal in the EPR spectra of our Mn implanted ZnO for higher Mn concentrations (red line in the EPR spectra of 8 at.% Mn implanted ZnO in figure 3), caused by dipole interaction of the closely spaced Mn ions within the implanted layer.

Thus, the total EPR spectrum consists of a fine structured contribution due to isolated, substitutional Mn$^{2+}$ ions in the substrate and a broadened, unstructured signal from dipole-interacting, substitutional Mn$^{2+}$ ions in the implanted layer.

### 4. Raman results and discussion

#### 4.1. Mn related additional modes: radiation damage, impurity-induced disorder and LVM

At the $\Gamma$-point of the Brillouin zone the optical phonons of the ZnO wurtzite lattice have the irreducible representation $\Gamma_{\text{opt}} = A_1 + 2B_1 + E_1 + 2E_2$ [15], with the $B_1$ modes being silent modes. The modes $A_1$ and $E_1$ are polar modes and therefore split into TO and LO phonons.

The most pronounced ZnO peaks in the majority of the spectra in figures 4–10 originate from the $E_2$(high) mode ($\sim 437$ cm$^{-1}$) and the two-phonon difference mode $E_2$(high)$–E_2$(low) ($\sim 333$ cm$^{-1}$), in accordance with the literature [15]. The other Raman active modes $E_2$(low), $A_1$(LO), $E_1$(LO), $A_1$(TO) and $E_1$(TO) lie at about 100, 574, 590, 378 and 410 cm$^{-1}$, respectively.

Figure 4 shows the Raman spectra of pure ZnO and ZnO implanted with 8 at.% Mn, compared to ZnO implanted with 8 at.% Co. In addition to the well-known ZnO $E_2$(high) mode, the main new features in the spectra of the ZnO:TM samples in figure 4 are observed in the range of 500–600 cm$^{-1}$. In the case of the Co implanted sample, a broad feature occurs at about 575 cm$^{-1}$. It can be assigned to the $A_1$(LO) mode of pure ZnO, intensified by TM implantation induced disorder. In the case of the Mn implanted sample, an additional shoulder is visible in this region at lower wavenumbers, controversially discussed in literature as partly or completely disorder related [5]–[13], [19]. As shown in figure 5, the intensity of the Raman signal in the range of 500–600 cm$^{-1}$ is directly correlated with the Mn concentration. We will show that two mechanisms participate in this effect. Firstly, the disorder generated by the radiation damage of the implantation process is of course higher for higher implantation concentrations. Secondly, there is the higher concentration of Mn ions in the ZnO crystal which can induce LVMs or disorder: Even if perfectly incorporated on Zn sites, the Mn ions induce disorder, inherent to the mixture of Zn and Mn on the cation sublattice.

To study the different contributions to the broad band in the Raman spectra, we conducted resonance measurements using different laser excitation wavelengths, as shown in figure 6. A strong rise in the relative intensity of the broad band is observed for laser lines with lower wavelengths. This can be explained by impurity activated Froehlich scattering [9, 20]. The resonance effect is particularly strong for the left of the two shoulders in the broad band.
Figure 4. From bottom to top: Raman spectra taken at 300 K from pure ZnO, 8 at.% Co implanted ZnO (700 °C annealing) and 8 at.% Mn implanted ZnO (700 °C annealing); excitation: $\lambda = 514.5$ nm.

Figure 5. From bottom to top: Raman spectra taken at 300 K from $x$ at.% Mn implanted ZnO for $x = 0.2, 0.8, 2.0$ and 8.0 after 700 °C annealing, normalized to the $E_2$ (high) mode; excitation: $\lambda = 514.5$ nm. The inset shows the intensity ratio $I_{A_1(LO)}/I_{E_2(\text{high})}$ versus the Mn concentration.

results support the hypothesis, that, besides the radiation damage effect, the Mn impurities play a major role in the formation of this broad band, especially for the left shoulder.

The above-mentioned two shoulder structure within the broad band between 500 and 600 cm$^{-1}$ can be identified in all spectra of the annealed Mn implanted ZnO samples. The right shoulder at about 575 cm$^{-1}$ is seen in ZnO:TM for a variety of different TM ions and can be
Figure 6. Raman spectra taken at 300 K from 8 at.% Mn implanted ZnO (700 °C annealing). The spectra were normalized to the E$_2$(high) mode; excitation from bottom to top: $\lambda = 632.8$, 514.5, 496.5 and 457.9 nm.

assigned to the disorder increased A$_1$(LO) mode of ZnO [14, 15, 21]. Our experiments on V, Fe, Ni and Co implanted layers also confirm this behaviour, see for example the Co implanted reference sample in figure 4. The effect is also seen in other ZnO samples with structural defects, e.g. in ZnO containing oxygen vacancies [22]. Therefore, we can state that this right shoulder is not specific to Mn incorporation. While there are several Raman features identified for ZnO:TM in this spectral region, the strong and broad left shoulder at about 520–530 cm$^{-1}$ is not observed for other TM in ZnO [9]–[11], [21, 23], see also the Raman spectra for Co implanted ZnO in figure 4. Also it is not known as a Raman signal of pure ZnO [14, 15]. Together with our results on the resonance behaviour of this shoulder, we can identify this feature as Mn related.

For a more detailed mode discussion of this spectral region, figure 7 provides the spectra of the 0.8 and 0.2 at.% Mn implanted ZnO after 700 °C annealing. The low Mn concentration and therefore lower disorder in those samples enable us to resolve separate modes instead of the broad unresolved band caused by the high phonon DOS in this region [24].

The features at about 437 cm$^{-1}$ (labelled a) and 575 cm$^{-1}$ (labelled e) were described above and can be attributed to the modes E$_2$(high) and A$_1$(LO). The mode at 438 cm$^{-1}$ (labelled b) can be assigned to a multi-phonon process of ZnO [15]. All features registered between 600 and 825 cm$^{-1}$, i.e. (f)–(k) in figure 7, are also seen in the measurements for the pure ZnO substrate and can therefore be explained by multiphonon processes of Raman active modes from pure ZnO [15]. Some of these multiphonon modes are stronger in intensity in the Mn implanted samples than for pure ZnO due to disorder effects and impurity induced resonance.

There are two more modes visible in figure 7: at about 519 and 537 cm$^{-1}$, denoted c and d, respectively. Note that the 537 cm$^{-1}$ mode also occurs for pure ZnO. Besides, Cusco et al. ascribe the mode at 537 cm$^{-1}$ to the 2 $\times$ B$_1$(low) or a 2 $\times$ LA process [15]. So from our data, we conclude that only the mode at about 519 cm$^{-1}$ cannot be explained by intrinsic ZnO modes. Interestingly, this feature significantly increases in intensity with rising Mn concentration from the 0.2 at.% sample to the 0.8 at.% sample.
Figure 7. From bottom to top: Raman spectra taken at 300 K from pure ZnO, 0.2 and 0.8 at.% Mn implanted ZnO (700 °C annealing), normalized to the $E_2$(high) mode; excitation: $\lambda = 514.5$ nm (Mn implanted ZnO) and $\lambda = 632.8$ nm (pure ZnO).

Figure 8. From bottom to top: Raman spectra taken at 300 K from pure ZnO, 8 at.% Mn implanted ZnO (700 °C annealing), bulk Zn$_{0.95}$Co$_{0.05}$O and bulk Zn$_{0.96}$Mn$_{0.04}$O; excitation: $\lambda = 514.5$ nm.

We now compare our implanted layer samples to a bulk Zn$_{0.96}$Mn$_{0.04}$O sample, grown by a vapour phase transport method at about 900 °C, which we now refer to as the ‘bulk’ sample. In contrast to the samples implanted with Mn concentrations $x \leq 0.8$ at.%, for this bulk Zn$_{0.96}$Mn$_{0.04}$O sample shown in figure 8 not only the $519$ cm$^{-1}$ (labelled c) mode but also a second additional feature can be identified in the left shoulder at about $527$ cm$^{-1}$ (labelled x). This additional feature is also indicated for the 8 at.% Mn implanted ZnO sample.
Figure 9. Raman spectra from bottom to top: pure ZnO and 8 at.% Mn implanted ZnO for different annealing steps (900 °C annealed, 700 °C annealed and unannealed); excitation: $\lambda = 514.5$ nm. The inset shows the $A_{1}(LO)$ mode position in dependence on the Mn concentration and the applied annealing steps.

The different growth process and the high growth temperature of the bulk sample could lead to a better substitutional incorporation of the Mn ions in the ZnO lattice. To study such temperature effects and to get information about the origin of the 527 cm$^{-1}$ and the 519 cm$^{-1}$ modes, we performed an annealing sequence for the implanted layers with temperatures up to 900 °C. Such annealing procedures are typically applied for implanted samples in order to heal radiation damage and to support a substitutional incorporation of the implanted ions. In pure but disordered ZnO, exhibiting a strong, disorder induced $A_{1}(LO)$ mode and a broadened $E_{2}$ (high) peak, annealing would improve the crystalline quality, and therefore the $A_{1}(LO)$ mode would be reduced and the half-width of the $E_{2}$ (high) phonon mode would become narrower. The commercial, pure ZnO substrate samples, used for the implantation in our experiments, are of excellent crystal quality and exhibit a very strong, narrow $E_{2}$ (high) mode and only a very small $A_{1}(LO)$ signal before implantation. Their crystal quality is not significantly improved by annealing, so the Raman spectra of these pure ZnO samples look identical without annealing, after 700 and 900 °C annealing, respectively. Figure 9 shows the 8 at.% Mn implanted sample not annealed, annealed for 15 min at 700 °C in air and additionally annealed for 15 min at 900 °C, respectively. For comparison, also pure ZnO is shown. The not annealed sample shows an extremely strong broad band between 500 and 600 cm$^{-1}$ with a dominating right shoulder. Its maximum is at about 560 cm$^{-1}$ and so about 14 cm$^{-1}$ away from the 574 cm$^{-1}$ position which can be expected for the $A_{1}(LO)$ mode in well ordered ZnO. We interpret the strong intensity of the $A_{1}(LO)$ mode and the shift to lower wavenumbers as a consequence of the radiation damage in this not annealed sample. In accordance with our result, similar mode shifts were observed before in ZnO with strong defects, e.g. oxygen deficiency [22]. Upon annealing at 700 °C the characteristic two shoulder structure can be seen. This effect is mostly due to the strong reduction of the broad $A_{1}(LO)$ mode.
This is confirmed by the second annealing step at 900 °C, which results in another strong reduction of the $A_1$(LO) structure. After this 900 °C annealing step, the left shoulder shows a slight shift to lower wavenumbers while approaching two feature behaviour (at about 519 cm$^{-1}$ and about 527 cm$^{-1}$) as identified for the bulk Zn$_{0.96}$Mn$_{0.04}$O sample in figure 8.

Both modes, at about 519 cm$^{-1}$ and 527 cm$^{-1}$, are reported in the literature for Mn alloyed ZnO. But to our knowledge there was no effort to distinguish between these modes, though both are equally taken as evidence for a substitutional incorporation of Mn on Zn sites [6, 12, 13, 19].

We believe that each of these modes has its own origin. The feature at 527 cm$^{-1}$ is strong in the Raman spectra of the more disordered samples with higher Mn content $1% \leq x \leq 4%$ (figures 4 and 5) and decreases upon annealing (figure 9). Besides, a mode at 528 cm$^{-1}$ is also observed in Sb alloyed ZnO [21, 25], evidence that it is no LVM, but probably a ZnO mode, activated or intensified by Mn ion incorporation. For example, Manjon et al calculated the $2 \times B_1$(low) mode to lie in this spectral region [26]. In contrast, the feature at 519 cm$^{-1}$ is covered by the broad disorder band in the spectra of highly disordered Mn alloyed ZnO and therefore it is only seen for our samples with Mn content $x \leq 0.8$ at. % or after thermal treatment up to 900 °C. The mode intensity scales with the Mn content in such well-ordered samples, as shown in figure 7 for the samples with $x = 0.2$ and 0.8 at.%. Also, our EPR experiments show for the annealed samples that the Mn ions are on Zn sites in the ZnO lattice, and therefore encourage the assumption that this mode is a candidate for a LVM of Mn substitutionally incorporated in ZnO.

But still there is a lack of theoretical backup for such a LVM hypothesis. To the best of our knowledge there are only very few theoretical studies of LVM by TM ions in ZnO [7, 27], which do not deliver a clear and consistent picture of the existence and frequency positions of such LVM. In summary, the overall intensity of the left shoulder at about 515–530 cm$^{-1}$ in the Raman spectra of ZnO:Mn should not be taken uncritically as evidence for a substitutional incorporation of Mn on Zn sites or for an estimation of the actual Mn content. Instead, the two different modes we identified within this shoulder have to be distinguished carefully. In future work, an enhanced theoretical understanding and also additional experimental methods, such as x-ray photoelectron spectroscopy (XPS) or x-ray absorption spectroscopy (XAS), could help to further clarify the exact origin of the identified additional Raman features.

4.2. Depth profile analysis of the Mn implanted layers

To study the depth profile of the Mn distribution and the associated disorder effects within the implanted layer we conducted a micro Raman scattering depth analysis. In this depth scan, we stepwise varied the laser spot position of the Raman microscope through the implanted layer and the underlying part of the substrate (total thickness about 0.5 mm). The absolute intensity of the various features in the Raman spectrum at the different steps of the depth scan is determined by the convolution of the response function of the sample and the optical detection profile (depth of field) of the microscope. The detection profile depth amounts to $6 \pm 0.5$ μm FWHM. In figure 10, the results of the depth scans are shown for the 8 at.% sample unannealed and after the second annealing step (900 °C), respectively. In all spectra the vertical scale is normalized to the ZnO $E_2$(high) mode intensity. This implies a strong stretching of up to 40 times for focus positions above the sample surface (negative depth values in figure 10). Stray light caused by diffuse reflection of the laser beam at the sample surface dominates the spectrum of the
unannealed sample for the focus depth of about $-4 \mu m$. Comparable stray light noise is not observed for the annealed samples. This confirms that the implantation damage on the surface and in the near surface region is strongly reduced by the applied annealing.

Deconvolution of the Raman depth scans confirms that the signals identified as implantation related derive from a near surface region. The spectra of the not annealed sample are dominated by the disorder intensified $A_1$(LO) mode. The spectra of the 900 $^\circ$C annealed sample show the two shoulder signature discussed above. Note that in the latter spectral series the Mn related left shoulder is particularly strong compared to the disorder related right shoulder, exactly at the focus depth for which the shoulder reaches its overall intensity maximum—a further indication that the two signals have a different origin and obviously also a different depth distribution. In figure 10 also a broad band between 900 and 1300 cm$^{-1}$ is visible which originates from second-order processes. To our knowledge this band was not discussed before in detail for Mn alloyed ZnO. It is dominated by features at about 1160, 1100 and 990 cm$^{-1}$, also reported for pure ZnO [15]. A broad feature evolves at about 1060 cm$^{-1}$ which does not occur in pure ZnO. Its intensity is correlated with the intensity of the feature at 527 cm$^{-1}$. Therefore, it is assigned to the second-order process of the 527 cm$^{-1}$ mode.

4.3. Secondary phase discussion

While substitutional Mn is crucial for the desired magnetic properties of the DMS $Zn_{1-x}Mn_xO$, one must also take into account the possibility of precipitate formation. Ferromagnetic $Mn_3O_4$ and anti-ferromagnetic elementary Mn or MnO can be reasons for the often contradictory reports of the magnetic properties of Mn substituted ZnO. In addition to the already mentioned XRD and TEM experiments, Raman spectroscopy offers a high potential for detecting
secondary phases. Its sensitivity can be attributed to its local probe character in contrast to
the long-range correlation requirement of interference based methods. This advantage was
confirmed in a direct comparison of Raman scattering and XRD on ZnO:Co by Wang et al [28].

In earlier studies, we identified the formation of Co$_3$O$_4$ and CoO, respectively, by Raman
scattering from their phonons for nanocrystalline ZnO:Co [29] and also for a Co implanted ZnO
sample. The predominating Raman modes for MnO, MnO$_2$, Mn$_2$O$_3$, ZnMn$_2$O$_4$ and Mn$_3$O$_4$ are
in the spectral range between 300 and 700 cm$^{-1}$ [30]. None of these modes could be identified
in the examined Mn implanted layers. This is in accordance with the results by TEM and XRD
(see section 3) and an important finding regarding the magnetic properties of the samples.
The antiferromagnetic coupling of the Mn on Zn sites, detected by EPR, can therefore be
attributed to Mn ions substitutionally incorporated on Zn sites in ZnO and not to the formation
of antiferromagnetic precipitates as elementary Mn or MnO.

An enhanced sensitivity for secondary phases can be expected in low temperature Raman
measurements due to more pronounced and sharper phonon peaks. However, for the examined
Mn implanted ZnO samples also Raman experiments at 10 K did not reveal any phonon
feature characteristic of secondary phase formation. Therefore, we conclude that the analysed
Mn implanted ZnO layers with $x \leq 8$ at.% are below the solubility limit of Mn in ZnO (in
accordance with literature results [31]) and no secondary phases are formed.

5. Conclusion

In our analysis of Mn-implanted ZnO neither for the unannealed nor for the annealed samples
were secondary phases observed by Raman scattering, XRD or TEM. The EPR results of the
annealed samples show a substitutional incorporation of Mn ions in the ZnO lattice and reveal
an antiferromagnetic dipolar interaction of the Mn ions.

Most features in the Raman spectra of the analysed Mn implanted ZnO samples were
identified as lattice modes of ZnO, intensified by Mn implantation induced disorder effects.
Features related to radiation damage on the one hand and Mn ion impurity on the other hand
were separated. The implantation damage is strongly reduced by the applied annealing steps
with temperatures up to 900 °C. The Mn impurity induced disorder within the implanted layer
is particularly strong for the 8 at.% sample and only partly healed with the applied annealing
procedures. We distinguished between two features in the spectral range often attributed to LVM
of Mn in ZnO. Only one of the observed modes (519 cm$^{-1}$) is a candidate for a LVM. So the
overall intensity of the left shoulder at about 515–530 cm$^{-1}$ in the Raman spectra of Mn alloyed
ZnO should not be taken uncritically as evidence for a substitutional incorporation of Mn on Zn
sites or even for an estimation of the actual Mn content.

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References

  Seshadri R 2005 Curr. Opin. Solid State Mater. Sci. 9 1–7
  Schneider J and Sircar S R 1962 Z. Naturf. A 17 651

Julien C M, Massot M and Poinsignon C 2004 Spectrochimica Acta A 60 689–700