Ferromagnetism and the oxygen vacancy in ZnO:(Mn,Co)

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Abstract

In this report the correlation between ferromagnetism and the oxygen vacancy in thin film ZnO doped with Mn and Co is investigated. This was done by annealing samples in both air and nitrogen and performing photoluminescence and VSM measurments. A weak ferromagnetic signal was observed in ZnO:Mn, the saturation value of which could be increased when annealed in nitrogen and decreased when annealed in air. The ZnO:Co samples however showed no ferromagnetic signals. The results from the Mn samples indicate that the oxygen vacancy does indeed play a part in the observed ferromagnetic response.

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1 Introduction

Transition metal (TM) doped ZnO along with GaN has been the focus of research over the past years owing to predictions of ferromagnetism with a Curie temperature above room temperature. If that is the case then this could eventually lead to quite interesting developments, such as spintronic devices. However there is still much uncertainty over whether these semiconductors actually exhibit ferromagnetism, which seems to be dependent on the growth and preparation techniques [5], and the more difficult question of what is the source of the magnetism.
Among the proposed models there are some that attribute the ferromagnetism to interactions between shallow donors, like the oxygen vacancy [3]. If the oxygen vacancy does play a part in the magnetic response then this can be investigated by annealing samples in oxygen rich environments thus reducing the number of vacancies, and also annealing in inert environments thus increasing their number.

2 Experiment

Two groups of TM doped ZnO were studied. First a group of Mn doped samples that were grown with molecular beam epitaxy (MBE) at 4% and 14% Mn concentrations on a sapphire substrate, additionally from the same growth run there was an undoped sample for comparison, these will from now on be referenced to as Mn4, Mn14 and Mn0, respectively. The second group of samples was Co doped and grown with plasma enhanced metalorganic vapor deposition (PE MOCVD) at 5%, 10%, 15% and 20% Co concentrations on a sapphire substrate. They will be referenced to as Co5, Co10, Co15 and Co20, respectively.

Photoluminescence measurments were performed by exciting with a 325nm He-Cd laser focused on the samples in a cryostat cooled to about 12K and using a SpectraPro 2300i spectograph. Magnetic response was measured with a Cryogenic mini high-field vibrating sample magnetometer (VSM) unit and the crystal structure was inspected with X-ray diffraction (XRD) measurments in a PANalytical's X'Pert PRO system.

3 Results

3.1 Mn-samples

3.1.1 XRD

Figure 1 show the results from the XRD mesurments for the Mn doped MBE samples. The observed peaks correspond to wurtzite ZnO along the [0 0 0 2] direction. Also present are a few smaller peaks that indicate the presence of some secondary phases. However, as they also appear in the undoped sample as well as the doped samples which indicates it's not a result of the doping. In the doped samples there is however a shift in the ZnO peaks to lower angles. The effect is greater in Mn14 than Mn4, which suggests that Mn atoms are taking the place of Zn atoms and changing the crystal lattice slightly.

Annealing Mn14 in nitrogen at 800 °C for 2 hours did not have a noticeable effect on the XRD results. When annealed in air under the same condition however there was a severe broadening of the peaks corresponding to ZnO, indicating a significant change in the crystal structure.

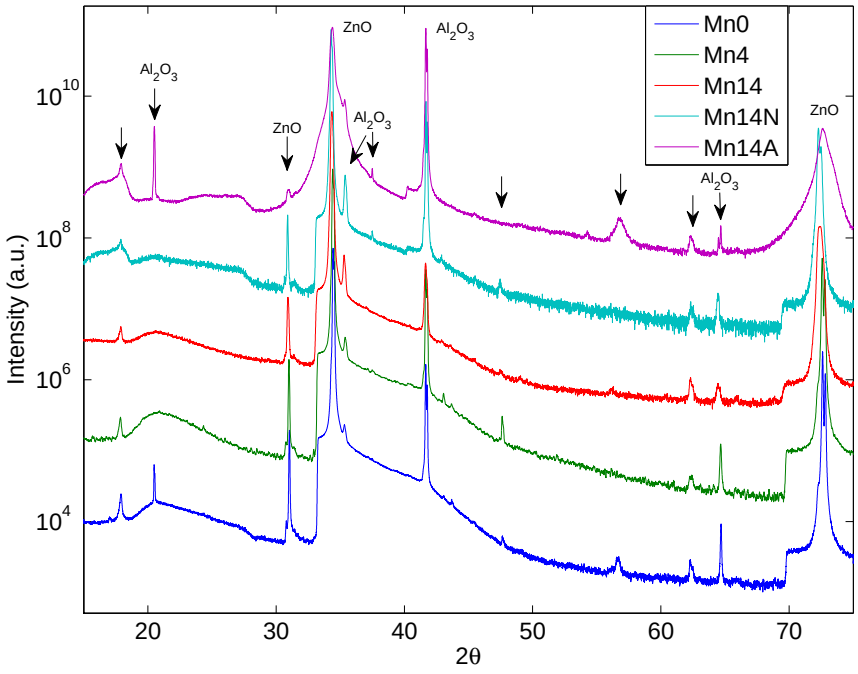

Figure 1: XRD results for Mn doped samples, where M14N and M14A have been annealed at 800 °C for 2 hours in nitrogen and air respectively

3.1.2 Photoluminescence

In the photoluminescence measurements there was some inhomogeneity both in the shape of the low-energy end and visibility of the band edge luminescence depending on where the exciting laser was focused. To make comparisons between the different samples the measurements were only made when the band edge luminescence was clearly visible. On Mn14 and Mn14N it was only in very few isolated spots while on Mn0, Mn4, and Mn14A it was visible over most of the sample.

In figure 2(a) the spectrum for the Mn samples can be seen. To compare the signals they have been scaled to the strongest peak detected in the band edge luminescence, corresponding to exitons bound to neutral donors, D^0X [9]. An additional peak can be seen in the band edge luminescence of Mn0 and Mn4 which is the phonon replica of D^0X. When the doping level is increased the intensity of the band edge and to a lesser extent the low-energy end decreases. It should be noted that in figure 2(a) the exposure of the Mn0 was considerably shorter than for Mn4 and Mn14 which were comparable in length.

In figure 2(b) there is a closer look at the low-energy end scaled to more easily compare the shape. Contributions from LO phonons [2, 8] in the low-energy end made fitting with gaussians difficult, so no fit is shown here. From simply looking at the shape of the curves it is easy to see that in Mn14A, which was annealed in air for 2 hours at 800 °C, that there is a considerable drop in intensity around 500nm, which corresponds to the approximate wavelength of the oxygen vacancy band. However for Mn14 and Mn14N, which were annealed in nitrogen for 2 hours at 800 °C, the shape is similar suggesting that Mn14 was already fairly rich in oxygen vacancies. This also corresponds to a color change of the samples that occured when annealed. Mn14N did not change but kept a reddish color, while Mn14A turned from reddish to green.

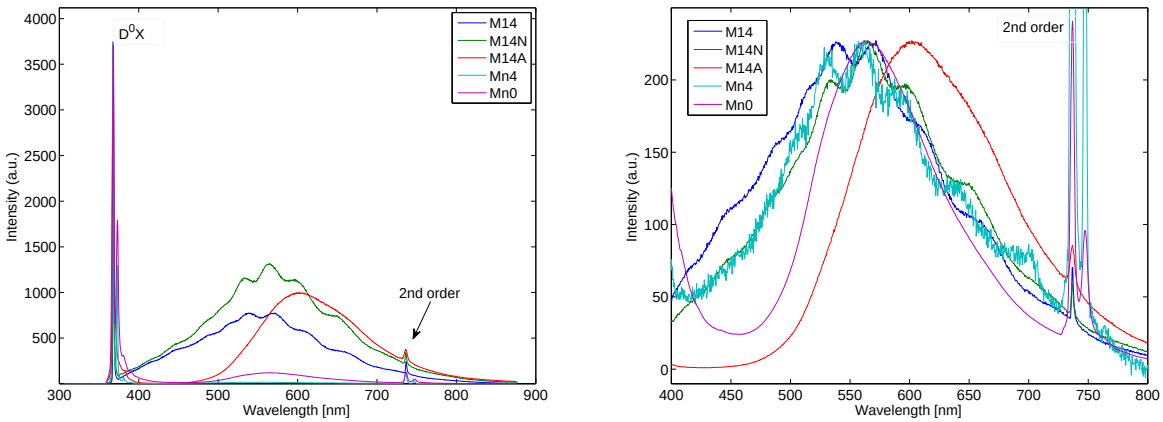

Figure 2: Left (a) : Spectra of Mn samples scaled to the D^0X peak. Right (b) : Same spectra focused on the low-energy end and scaled to compare the curves.

3.1.3 Magnetism

The only sample that showed clear ferromagnetic behavior was Mn14. It had a signal that was measurable up to 300K, which means that the Curie temperature is above room temperature. In figure 3 the results of annealing the Mn14 sample can be seen. When annealed in air the signal completely disappears while it increases by up to roughly 60% when annealed in nitrogen.

There were some problems with reproducibility of the annealing. The signal did not always increase, but seemed to be sensitive to both annealing duration and temperature. A possible reason might be that the untreated samples were already rich in oxygen vacancies, so annealing in nitrogen would not have a great effect. The effect of duration and temperature could not be fully studied for the lack of sufficient number of samples. This gives, however, indication that the ferromagnetism is related to the oxygen vacancy.

The conclusion is not necessarily definitive since there have been reports of similar results [6], but also opposite ones [7] where annealing in air increased the saturation and annealing in nitrogen decreased it. There have also been reports of no ferromagnetism at all [1], as was also seen in Mn4. This suggests that the growth technique and doping concentration play an important part in the ferromagnetic response in TM doped ZnO.

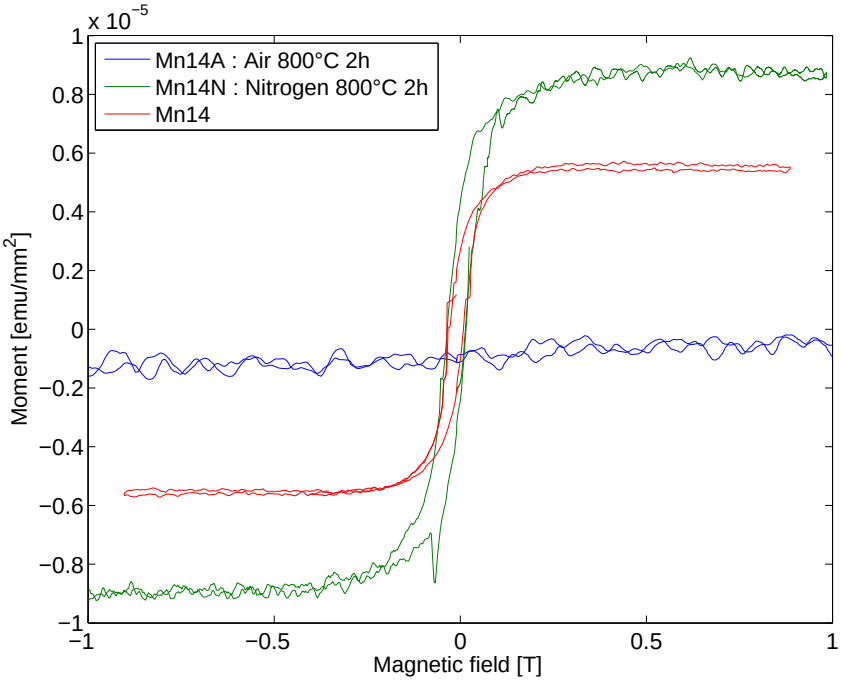

Figure 3: Magnetism results for Mn14, Mn14N and Mn14A, diamagnetic tail has been removed.

3.2 Co-samples

3.2.1 XRD

Figure 4 shows the results for the Co samples in XRD. Included is also a measurment of a pulsed laser deposition (PLD) grown ZnO sample for reference. No peaks corresponding to wurtzite ZnO are detected with the exception of Co10 where there is a small hint of it but it is much weaker than the substrate peak. This along with some visible inhomogeneity of the sample films, especially Co5 where parts of the film seem to be missing, indicates that something may have gone wrong with the growth process.

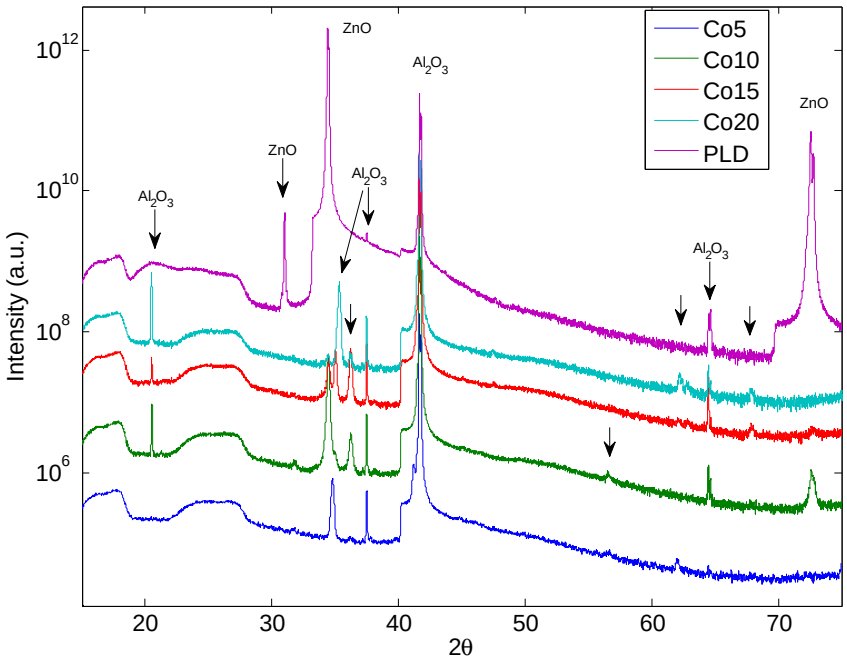

Figure 4: XRD results for Co doped samples, as well as a PLD grown ZnO sample for comparison.

3.2.2 Photoluminescence

As was with Mn14, detection of the band edge luminescence was difficult as it only appeared in small isolated spots. In figure 5(a) the spectra can be seen for the Co samples, scaled to the D^0X peak. There is a very definitive structure that starts at 660nm which is attributed to the Co^{2+} *d*-levels interaction [10]. Figure 5(b) is scaled to the peak starting at 660nm. The only notable change is that Co20 has a much weaker band edge compered to Co5 and Co15. This is similar to what was observed with the Mn samples where the band edge luminescence diminishes with increased doping. The shape of the low-energy end is fairly similar between the diffirent Co samples.

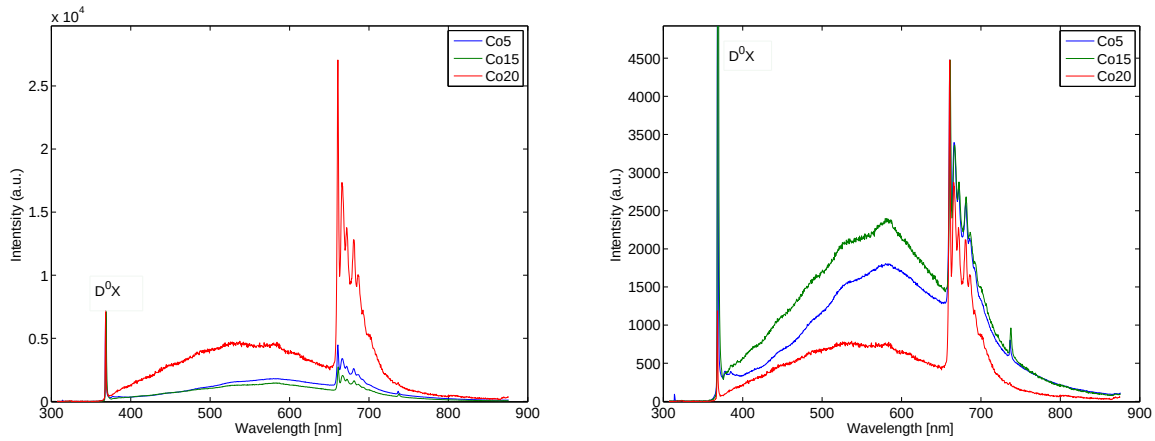

Figure 5: Left (a) : Spectra of Co samples scaled to the D^0X peak. Right (b) : Same spectra but scaled to the 660nm peak.

3.2.3 Magnetisation

No ferromagnetic signal was detected from any of the Co samples. Attempts at annealing Co20 and Co15 in nitrogen resulted in no change to the signal. Testing whether the samples were paramagnetic was made impossible because of a problem with the VSM. Hence there was no way to subtract the diamagnetic signal from the substrate and sample holder to investigate this.

4 Conclusions

Having investigated the correlation between ferromagnetism and the oxygen vacancy there seems to be a link between them when a ferromagnetic signal is actually achieved. However, achieving this signal seems to depend on growth techniques and doping concentration. The only sample exhibiting a ferromagnetic signal was the 14% Mn doped sample. When annealed in nitrogen the signal increased but annealing in air it decreased. No ferromagnetic signal was detected in 4% Mn doped or any of the Co doped samples.

A further study of the effects of duration and temperature dependance of the annealing process with a larger and more varied supply of samples along with a more detailed characterization of defects would be a good step to better understanding the relation between the oxygen vacancy and ferromagnetism in TM doped ZnO.

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