Clusters in Cobalt implated Boron pre-doped ZnO

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Diluted magnetic semiconductors (DMS) have attracted a lot of interest for spintronic application. Co-implanted ZnO is one of the promising ferromagnetic DMS. It has been demonstrated earlier [1] that co-doping helps to enhance the magnetic property by forming beneficial compositions. Simultaneously, also useless compositions come into being. Taking into account this aspect, here we performed a systematic structural investigation of the pre-doped Co-implanted ZnO. In particular, we focus on the effect of B pre-doping on n-typ ZnO.

30 keV B^+ ions were implanted (fluences ranges from 5×10^{15} to 3.2×10^{17} cm^{-2}) with a 7° tilt from the surface normal into a hydrothermally grown (0001)ZnO which was mounted on a holder cooled by liquid nitrogen. Considering sputtering the maximum of the depth profile is calculated to be at 40 nm (Fig. 1). Subsequently, 80 keV Co^+ ions were implanted using the same angle and cooling but with a single fluence of 8×10^{16} cm^{-2} giving an almost box like profile (Fig. 1 and 2).

As apparent from Fig. 3, the surface layer is mostly amorphized by implantation but a close inspection reveals the presence of fractions of crystalline material. This layer is broardened by increasing B^+ fluence and reaches a maximum depth of ~120 nm. Concerning the magnetic properties, the sample corresponding to the highest fluence is of most interest and therefore it is only considered here.

Using diffraction patterns (not shown here) a set of appropriate compositions can be extracted as constituents of the layer modified by B pre-doping and Co implantation: a) ZnO itself, b) fcc $ZnCo_2O_4$, c) fcc CoO SG216, d) fcc CoO SG225, e) hex Co, f) fcc Co. Because of too many commensurate interplanar distances it cannot be decided on the base of these diffraction patterns which of the compositions really exist. As demonstrated in the following high resolution imaging and subsequent Fast Fourier Transform of singular grains is the way to overcome this problem.

As shown in Fig. 3 big (>15nm), medium, and small (<5nm) sized clusters embedded in amorphous surroundings could be observed. On top of the layer small rests of pure ZnO were found (a). Corresponding to the Co profile (Fig. 1) in a depth of 20 to 50 nm small amorphous Co clusters exist (exemplary labeled by one circle). Those clusters were assumed to be mainly responsible for the magnetic properties plus a small contribution from paracrystalline $ZnCo_2O_4$ clusters. Detectable in the same depth they are known as superparamagnetic clusters arising after high fluence implantation [2]. Moreover, $ZnCo_2O_4$ clusters of the same size were found in the depth > 60 nm (b) being crystalline (big cluster in Fig. 4). Additionally, in a depth > 70 nm a few medium sized clusters were observed. One fraction could be indicated as fcc CoO (c) (SG216) (CoO (SG225) could not be evaluated). Another fraction corresponds to pure Co. Here, both the hex (e) and the fcc (f) type have been taken into consideration..

1. T.C. Kaspar et al., Phys. Rev. B **77**, (2008) p201303(R).
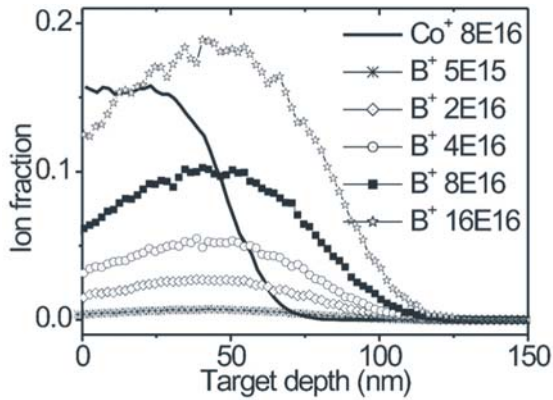2. K. Potzger et al., Appl. Phys. Lett. **93** (2008) p232504.

Figure 1. TRIDYN simulation displaying the expected depth profiles of the implanted ions (sputtering considered)
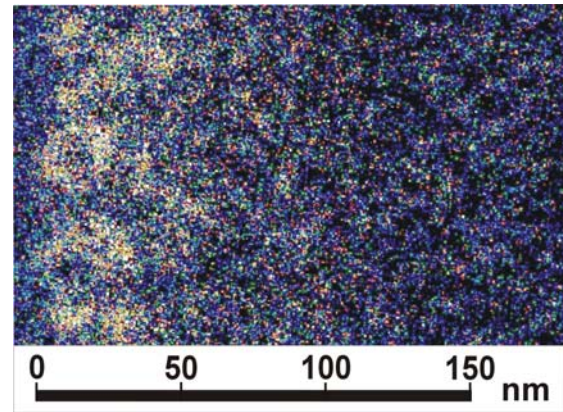

Figure 2. EFTEM image (CoM2,3 edge) exemplarily taken for the sample representing the state of the highest B$^+$ fluence

a) hex ZnO

b) fcc ZnCo$_2$O$_4$

c) fcc CoO SG216
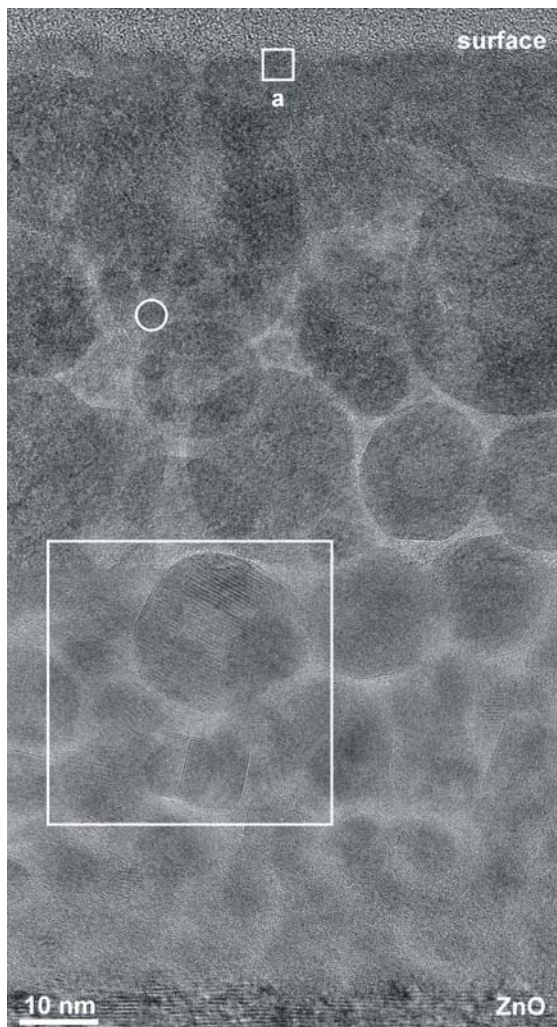
(d) fcc CoO SG225)

e) hex Co

f) fcc Co

Figure 3. Montage of two HRTEM images showing the amorphized and largely recrystallized near surface layer which contains compositions listed on the right
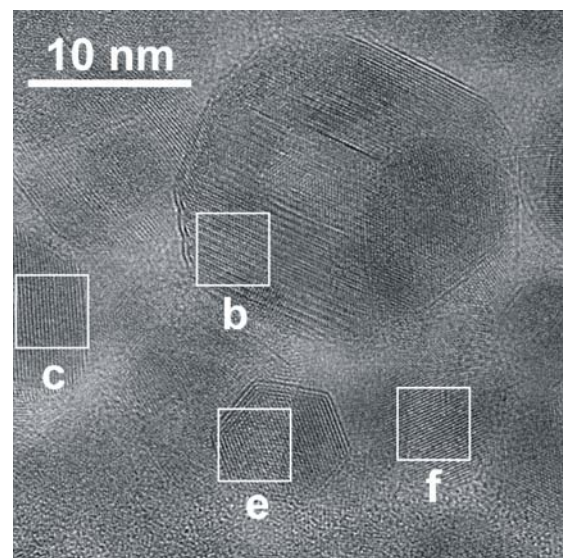
Figure 4. Inset of Fig. 3 (focus slightly changed) showing in more detail where which of the compositions listed above has been found in greater depth