

The Evaluation of p-type doping in ZnO taking Co as dopant

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Abstract: P-type doping is excessively difficult in wide-band gap semiconductors, such as GaN, ZnSe, and indeed ZnO. Practically it is very difficult to obtain stable and true p-type ZnO. Under standard conditions there are reports on decaying or even completely absent p-type conductivity. Several hypotheses have been formulated to explain this unusual behaviour. The commonly accepted theory is that the elements assume undesired (non-substitutional) positions or form complexes, resulting in self-compensation of the p-type conductivity. Note that p-dopants can be compensated by low energy native defects, such as Zni or VO, or background impurities, such as aforementioned H. Deep impurity levels can cause significant resistance to the formation of a shallow acceptor level. In this work the p-type doped ZnO based samples are prepared where incorporation of Co into the ZnO crystal lattice is done and various measurements like Sheet resistivity, Hall Voltage, Hall mobility and 2d hole concentration are made. From the results it has been clearly found that the p-type doping takes place successfully and can be used for various future applications.

Keywords. Hall Voltage, Dopant, Semiconductors, Hall mobility

I. Introduction

The studies on ZnO started at the beginning of 1950. But the attention is slackened up to the middle of 1990, because the epitaxial growth of ZnO is difficult and the p-type doping did not succeed. n- and p-type conduction is necessary for electronic applications like diodes and bipolar transistors[1-4]. Since middle of 1990's there is an increasing interest because of the hope for an alternative material to GaN, which is the main material of commercially available light emitting and laser diodes in the blue and UV spectrum [1]. The processing of GaN[5] and ZnO is not easy, their band-gaps are nearly equal, but ZnO has a significant higher exciton binding energy of 60 meV which facilitates many electrical and optical applications[5-7]. Additionally, magnetic ions like Co can be incorporated into ZnO to make it magnetic and prepare it as a material for spintronics. So, ZnO is a promising candidate to realize a diluted magnetic material, and actually with Curie temperature above room temperature[5-6]. There is thus a high interest to achieve reproducible p-type doping also in ZnO.

Practically it is very difficult to obtain stable and true p-type ZnO[7-10,15]. Authors report on decaying [7, 11] or even completely absent [5] p-type conductivity under standard conditions. Several hypotheses[11-13] have been formulated to explain this unusual behaviour. The commonly accepted theory is that the elements assume undesired (non-substitutional) positions or form complexes, resulting in self-compensation of the p-type conductivity [6,14]. Other theories include lattice relaxation effects or low solubility of the target dopant in the matrix, as mentioned by Claflin et al. [5]. Recently several authors have successfully obtained stable p-type ZnO by codoping, i.e. adding an n- and p-type dopant to the ZnO. For example Tang et al. [7] adds 0.4% Al as well as N, creating p-type material, whereas adding 1% Al would make it n-type. It is believed that the addition of Al stabilises or at least eases the formation of ionised N acceptor levels [15].

In this work the p-type doped ZnO based samples are prepared where incorporation of Co into the ZnO crystal lattice is performed and various measurements like Sheet resistivity, Hall Voltage, Hall mobility and 2d hole concentration are made. From the results it has been clearly found that the p-type doping takes place successfully and can be used for various future applications.

II. Experimental

The sapphire-substrate is annealed at 500°C for 3 hours in a high-vacuum sputtering chamber with a base pressure of 1×10^{-7} mbar and etched for 10 min with an Ar ion beam before the deposition of ZnO. The selected properties of ZnO[16] are shown in table 1. The ZnO layer with a nominal thickness of about 20 nm, according to the deposition time, is grown by sputter on single-crystalline oriented a-plane Al₂O₃ (sapphire) wafer, of which both sides are polished. RF(13.56 MHz) sputtering is performed in an atmosphere of 5×10^{-3} mbar pure Ar(99.999%) at 500°C. In order to increase the crystallinity of the ZnO films, a post-growth annealing process is carried out in an oxygen atmosphere with a partial pressure of up to 2000 mbar and a temperature of 800°C. After annealing, ZnO samples are implanted in ILU-3 ion accelerator (KPTI

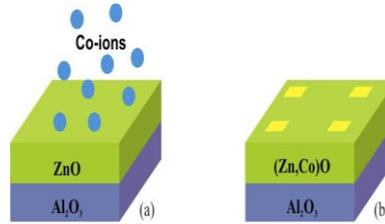
of RAS) with 40 keV Co⁺ ions at doses ranging from 0.25x10¹⁷ ions/cm² to 2.00x10¹⁷ ions/cm², at an ion current density of 8 μA/cm².

For Hall measurements in vander Pauw geometry, four Au contacts are evaporated, of which the I(V) characteristics exhibits an ohmic behavior, and have resistances ranging from 100 Ω to 1 kΩ determined by Hall measurement in which magneto transport measurements are performed in two point geometry with a magnetic field H perpendicular to the sample plane. The layer structure and the Au contacts are shown in figure 1.

Fig.1. Co⁺ ions are implanted at various doses into ZnO grown on a-plane sapphire (a). Au contacts are realized (b).

Table 1: The selected Properties of ZnO.

Group	II-VI Compound
Crystal structure	Rocksalt(B1),Zinc Blende(B2), Wurtzite(B3)
Atomic weight	81.38 amu
Lattice Constant	4.580 Å ⁰
Density	5.67 gm/cm ³
Eg(300K/0K)	3.35ev/3.42ev
Band Gap Type	Direct
Electron mobility	200 cm ² /Vs
Hole mobility	180 cm ² /Vs
Effective mass m*/m ₀	0.27
Intrinsic carrier Conc.n _i	7.0X10 ¹⁶ cm ³
Donors	Al, Ga,In,Cl,I
Acceptors	Li, Na, K, Co,N,P,As



III. Results and Discussion

The Hall data for Co-implanted ZnO samples with different doses are summarized in table 2 and table 3. These measurements are executed several times and the results are reproducible. For the lowest two doses (0.25X10¹⁷ ions/cm², 0.50X10¹⁷ ions/cm²) and for the highest one (2.00X10¹⁷ ions/cm²), the measurements cannot be made because of a too small signal-to-noise ratio of the Hall voltage. For all other doses, a positive Hall voltage is measured, which clearly indicates that the material is p-type.

Table 2: Hall data of the samples Z1(D = 0.75X10¹⁷ions/cm²),Z2(D=1.0X10¹⁷ions/cm²), and Z3(D=1.25X10¹⁷ions/cm²) at RT are summarized. D is the implantation dose.

Features	Z1	Z2	Z3
Sheet resistivity [Ω]	245	69	132
Hall voltage [μV]	587	480	48
Hallmobility[cm ² /Vs]	45	87	68
2D hole concentration [cm ⁻²]	5.7x10 ¹⁴	1.0x10 ¹⁵	6.9x10 ¹⁴

Table 3: Hall data of the sample Z4 at RT and 4.2 K are summarized, where the implantation dose is 1.50x10¹⁷ ions/cm².

Temperature[K]	300	4.2
Sheet resistivity[Ω]	55	48
Hall voltage[μV]	7	5
Hall mobility[cm ² /Vs]	172	91
2D hole concentration[cm ⁻²]	6.7X10 ¹⁴	1.5X10 ¹⁵

From the above tables clearly the 2D hole concentration increases with increasing implantation dose, which is an indicator to the incorporation of Co into the ZnO crystal lattice as shown in fig.2.

However, in order to be sure that this results are trustable, anomalous Hall measurements are performed. Because, at lower magnetic fields the behavior of the Hall voltage is determined by both ordinary and anomalous Hall terms. Thus a confident measurement has to do above the saturation field where the Hall voltage depends directly on the magnetic field, if the sample is ferromagnetic as the samples Z1-Z3. If the slope of the V_H -B curve is negative, there is an electron conduction, and a positive slope indicates a hole conduction. Fig.3 shows the results of the anomalous Hall measurements. The Positive slope shows clearly that the conduction material is hole but also note that there is a negative slope at the saturation field showing that the formed material system also consists electrons of density about $2 \times 10^{15} \text{ cm}^{-2}$.

As mentioned previously, p-type doping of wide-band-gap semiconductors (ZnO, GaN, ZnSe,...) is very difficult. The difficulties can arise from various reasons. Dopants may be compensated by low-energy native defects, such as Zn_i (Zn interstitials). Low solubility of the dopant in the host material is another possible reason. Deep impurity levels can also be a source of doping problem causing significant resistance to the formation of shallow acceptor level. But here the formation of P-type doped ZnO is successful.

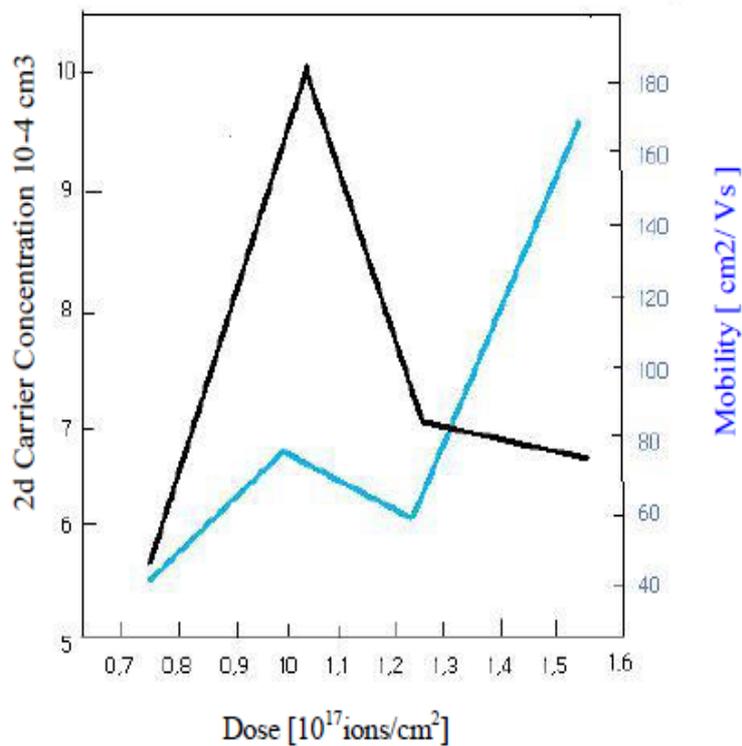


Fig 2: The 2D hole concentration and the mobility as a function of implantation dose.

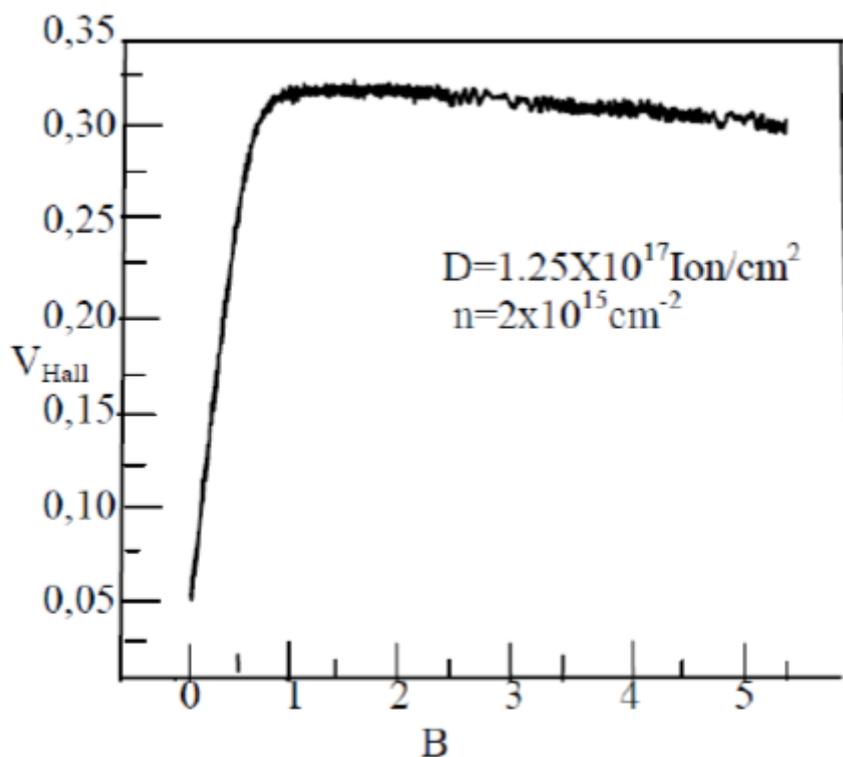


Fig.3: The anomalous Hall effect on the sample Z3 observed at 4.2 K. D is the implantation dose of the ions and n is the electron density.

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