Activities towards $p$-type doping of ZnO

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Abstract. Zinc oxide (ZnO) is an interesting and promising semiconductor material for many potential applications, e.g. in opto-electronics and for sensor devices. However, its $p$-type doping represents a challenging problem, and the physical reasons of its mostly $n$-type conductivity are not perfectly clear at present. Efforts to achieve $p$-type conductivity by ion implantation are reviewed, and ways to achieve $p$-type ZnO nanorods and thin films through various growth conditions are summarized. Then, issues associated with the preparation of Schottky contacts is discussed in some detail as this is a requirement of the device formation process. Finally, the possible incorporation of hydrogen and nitrogen into structural defects, which can act as trapping sites for positrons, is discussed in the context of experimental and theoretical positron results and the estimated H and N content in a variety of ZnO materials.

1. Introduction

Zinc oxide (ZnO) is an interesting and promising semiconductor material for many potential applications, e.g. in opto-electronics and for sensor devices [1-4]. The interplay of dopants, impurities, and intrinsic defects is essential for the electrical and optical properties of ZnO, especially if one would like to achieve $p$-type conductivity.

In a recent approach for $p$-type doping by repeated temperature modulation growth [5] it has been shown exemplarily that high quality crystal growth and doping with nitrogen have to be done in rather different temperature regimes. On the other hand, ion implantation with nitrogen into commercially available ZnO single crystals and subsequent thermal annealing has also been demonstrated to result in the creation of a $p$-$n$ junction and electroluminescence [6, 7]. However, in any case defect creation and dopant incorporation remain to be studied systematically, if possible with methods rendering structural information on an atomistic level.

Positron Annihilation Spectroscopy (PAS) [8, 9], especially in the form of Slow Positron Annihilation Spectroscopy (SPIS) using mono-energetic positrons [10], is now a well-established tool for the study of electronic and defect properties of bulk solids and thin films. In particular, it can primarily reveal information about open-volume defects and their chemical surrounding provided they are not positively charged. Temperature-dependent measurements may also reveal some information about the presence of shallow positron traps, like interstitial impurity ions, but the interpretation of experimental data is not straightforward and more difficult.
A consistent theoretical modeling of bulk and defect positron properties of ZnO with and without lattice relaxation has been published for the first time only recently [11] including a summary of all types of PAS studies published so far. All positron lifetime data available in the literature have been collected [12] and related to the values calculated for bulk and defect configurations within the same scheme presented in Ref. [11]. From this comparison, the idea of the existence of $V_{\text{Zn}}$ – hydrogen complexes in ZnO sampled by positrons was born.

A very systematic study of various, nominally undoped ZnO single crystals, either hydrothermally grown (HTG) or melt grown (MG), has been performed [13]. The crystal quality has been assessed by X-ray diffraction (XRD), and a comprehensive estimation of the detailed impurity and hydrogen contents by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Nuclear Reaction Analysis (NRA), respectively, has also been made. High precision positron lifetime experiments then showed that a single positron lifetime is observed in all crystals investigated, clustering at 180-182 ps and 165-167 ps for HTG and MG crystals, respectively. Furthermore, hydrogen has been detected in all crystals in a bound state with a high concentration (at least 0.3 at.-%), whereas the concentrations of other impurities have been found to be comparatively very small. From ab initio calculations it is suggested that the existence of Zn vacancy-hydrogen complexes is the most natural explanation for the given experimental facts at present. All experimental findings imply that the role of H in ZnO is yet far from being completely understood, and that various types of Zn vacancy-hydrogen complexes need to be taken into account in future studies.

Nitrogen substituting oxygen (N$_{\text{O}}$) and N$_2^-$ molecules have been identified in ZnO by Electron Paramagnetic Resonance (EPR) [14, 15]. Complex centres containing nitrogen and Zn interstitial (Zn$_i$-N$_{\text{O}}$) atoms [16] and “pure” intrinsic defects created by low temperature, high-energy electron irradiation [17] have been observed by optically detected magnetic resonance. The influence of nitrogen on the lattice dynamics of ZnO has also been investigated in a series of samples grown by Chemical Vapour Deposition (CVD) containing different nitrogen concentrations, as determined by Secondary Ion Mass Spectroscopy (SIMS) [18]. The Raman spectra revealed several local vibrational modes (LVM’s) in addition to the host phonons of ZnO, and their intensity has been found to correlate linearly with the nitrogen concentration. This fact has been used as a quantitative measure of nitrogen in ZnO. Furthermore, SIMS has shown that a correlation also exists between the concentration of incorporated N and unintentional H, similar to the incorporation of the $p$-dopant Mg and H in GaN during metal-organic CVD (MOCVD) [19].

Experimental investigations on CVD grown, N-doped ZnO [20-23] revealed that these samples contain not only a large amount of H, but also C, as well as an excess of N in unwanted forms. These works also provide some insight into the difficulties of creating $p$-type ZnO through the incorporation of nitrogen, and suggest that these defects may play important roles in compensating or passivating the N acceptors. Moreover, infra-red (IR) absorption measurements on N-doped ZnO showed several peaks in the range of 1800–2000 cm$^{-1}$, which are surprisingly close to the IR frequencies of free diatomic molecules but significantly higher than the phonon frequencies of the ZnO host.

In a theoretical work [24], real-space multi-grid electronic structure calculations within the local-density-functional approximation have been exploited to find out a mechanism for the compensation of N acceptors in ZnO which could explain the difficulty in achieving low-resistivity $p$-type ZnO. There, it has been found that at low N doping levels using a normal N$_2$ source, O vacancies are the main compensating donors for N acceptors, while N acceptors are compensated via the formation of defect complexes with Zn anti-sites at high doping levels. When an active plasma N$_2$ gas is used to increase the N solubility, N acceptors are still greatly compensated by N$_2$ molecules at oxygen sites and N-acceptor-N$_2$ complexes.

First-principles calculations [25] have shown that $AB$ defects substituting on an O site in ZnO, where $A, B = N, O, \text{or} C$, are an important class of defects whose physical properties cannot be described by the usual split interstitials but rather by substitutional diatomic molecules. The molecular nature of the $(AB)_0$ defects are reflected in their vibrational frequencies, which are red-shifted from those of the corresponding free molecules – but only by about 10%. These calculated results agree
with the frequency range observed by IR measurement on N-doped ZnO [20-23]. Moreover, most $(\text{AB})_\text{O}$ defects are donors in $p$-type samples. The $(\text{NC})_\text{O}$ and $(\text{N}_2)_\text{O}$ defects have been found to have sufficiently low energies to convert substitutional $\text{N}_\text{O}$ acceptors into donors, thereby hindering the efforts of doping ZnO $p$-type.

Engineering of the optical band gap of ZnO has already been demonstrated, e.g. by shifting to higher or lower energy by alloying with MgO [26-28], or CdO [29, 30], respectively. In a more recent work [31], Raman measurements have indicated an increased solubility of N in MgZnO compared with that in ZnO. Using first-principles band structure methods, the formation energy and transition energy level for the nitrogen acceptor in ZnO and a randomly chosen Mg$_x$Zn$_{1-x}$O alloy (with $x = 0.25$) have been calculated. The results support the experimental findings and point out that the acceptor energy level deeper in the alloy can be ascribed to the downward shift of the valence-band maximum edge in the presence of magnesium.

It is certain that all types of applications rely on a full understanding of the role of lattice defects in ZnO, and provision of high-quality bulk material, films, and also nanostructures. However, its $p$-type doping represents a challenging problem, and the physical reasons of its mostly $n$-type conductivity are not perfectly clear at present.

In the present work, three different activities will be summarized. First, efforts to achieve $p$-type conductivity by ion implantation are reviewed, and the creation of a $p-n$ junction by $\text{N}^+$ ion implantation and thermal annealing is discussed. Second, ways to achieve $p$-type ZnO of thin films and nanorods by various growth conditions are presented. Third, the preparation of Schottky contacts on ZnO is discussed in some detail as this is a serious requirement of the device formation process. Finally, the possible incorporation of hydrogen and nitrogen into structural defects, which can act as trapping sites for positrons, is considered. This latter issue will be discussed in the context of experimental and theoretical positron results and the estimated H and N contents in a selected variety of ZnO materials.

2. Activities to achieve $p$-type ZnO

2.1. Ion implantation

The creation of semiconductor devices is mainly based on ion implantation as a primary step to create $p-n$ junctions because this method allows tailoring their depth in the material and geometrical structure in accordance with industrial production needs. However, the implantation is unavoidably connected with the creation of point defects (extrinsic defects) which might be removed by post-implantation annealing. But the material of choice for doping by ion implantation may already possess intrinsic defects which are mainly determined from the growth conditions, like the impurity content and lattice defects. On the other hand, electrical activation of dopant atoms after implantation also requires thermal annealing at higher temperatures. The time spent by the implanted material at the annealing temperature will allow diffusion of the defects and dopant atoms as well. Thus, it is necessary to characterize any material regarding its defects, and to investigate their annealing in order to optimize the annealing conditions for a given material.

Possible ways for achieving $p$-type conductivity of ZnO are shown in figure 1 as a schematic illustration. First, doping by ion implantation will be considered.

Based on first-principles calculations, a method for fabricating $p$-type ZnO with group-I elements such as Li and Na has been suggested [32]. It has been found that with group-I dopants alone, substitutional acceptors are mostly self-compensated by interstitial donors, whereas in ZnO co-doped with H impurities, the formation of compensating interstitials is severely suppressed, and thus the acceptor solubility is greatly enhanced by forming H-acceptor complexes. Then, H atoms could be easily dissociated from these defect complexes at relatively low annealing temperatures, and thus low resistivity $p$-type ZnO would be achievable with dopants different from group-V elements.
Other authors present their first-principles calculations of doping effects in ZnO with group-IB elements, such as Cu, Ag, and Au [33]. The calculated transition energies for substitutional Cu, Ag, and Au have been estimated to be very low for these group-IB elements on the substitutional sites, but rather high at the interstitial sites under oxygen-rich growth conditions. Under these conditions, the formation of major hole-killer defects, such as oxygen vacancies ($V_O$) and Zn interstitials (Zn$_i$), will be suppressed. Thus, Ag has been suggested to may be a good candidate for producing $p$-type ZnO.

Based on first-principles calculations, a model for large-size-mismatched group-V dopants in ZnO has also been proposed [34]. The dopants have been found to not occupying the O sites as is widely perceived, but rather the Zn sites: each forms a complex with two spontaneously induced Zn vacancies ($V_{Zn}$) in a process that involves fivefold As coordination. Moreover, an As$_{5e}$-2$V_{Zn}$ complex has been estimated to have maybe lower formation energy than any of the parent defects. The model agrees with the recent observations that both As and Sb have low acceptor-ionization energies and that to obtain $p$-type ZnO requires O-rich growth or annealing conditions. Interestingly, $p$-type conductivity in ZnO with exceptionally large-size-mismatched dopants such as P [35], As [36, 37], and Sb [38] has already been reported.

Ion implantation with nitrogen, having an ionic radius comparable to oxygen, into commercially available ZnO single crystals and subsequent thermal annealing has already been shown to result in the creation of a $p$-$n$ junction [6, 7]. The rectifying property of the $p$-$n$ junction was found to persist after the annealing temperature up to 1200 °C [7]. With the fabrication of a 50 nm indium-tin oxide (ITO) $n^+$-film on top of the $p$-layer, the diode under a forward bias emitted light at room temperature [7]. The luminescence intensity increased with increasing forward bias voltage and the electroluminescence spectra showed peaks at ~530 nm (~2.34 eV) and ~740 nm (~1.68 eV). A Deep Level Transient Spectroscopy (DLTS) study on the N$^+$-implanted ZnO diode showed that the ion implantation had the effects of introducing a deep level at $E_C$=–0.95 eV (D1) and enhancing the intensity of another deep level $E_C$=–0.30 eV (E3), which originally existed in the as-grown sample [7]. D1 and E3 disappeared after the annealing at 750 °C and 900 °C, respectively [7]. After annealing at 750 °C, another trap having the activation energy of 0.17 eV (D2) was formed [7].

Second, for an understanding of $n$-type conductivity of ZnO, the role of intrinsic defects – i.e. native defects which are a result of the growth conditions and impurity atoms of the given ZnO material – would be invaluable in the design of a treatment to achieve tailored $p$-type conductivity. However, in spite of extensive research for many years the role of these intrinsic defects is still not perfectly clear at present.

![Figure 1. Cartoon showing how to achieve $p$-type conductivity of ZnO, by courtesy of Matthias Schmidt (U Leipzig).](image-url)
Using first-principles methods based on density functional theory and pseudopotentials, a detailed study of native point defects in ZnO has been performed recently [39]. Contrary to the conventional wisdom, it has been estimated that native point defects are unlikely to be the cause of the frequently observed unintentional \( n \)-type conductivity. \( V_0 \) defects, which have most often been invoked as shallow donors, have been found to possess high formation energies in \( n \)-type ZnO, and thus are actually deep donors with very high ionization energy. \( Zn_i \) defects have been calculated to be shallow donors, but to have high formation energies in \( n \)-type ZnO; in addition, they are fast diffusers, and thus unlikely to be stable in \( n \)-type ZnO. \( Zn \) antisites (\( Zn_o \)) have been found to possess high formation energies in \( n \)-type ZnO, and thus are actually deep donors with very high ionization energy. \( V_0 \) defects have been estimated to be deep acceptors which may act as compensating centres in \( n \)-type ZnO. Oxygen interstitials (\( O_i \)) have been calculated to be stable in the form of electrically inactive split interstitials as well as deep acceptors at the octahedral interstitial site under \( n \)-type conditions. These results [39] provide a guide to more in-depth experimental studies of point defects in ZnO and their influence on the control of doping.

A comprehensive discussion of results from PAS studies aimed at the identification of structural defects, both intrinsic and extrinsic, can be found in Refs. [11-13].

Investigations of intrinsic defects in ZnO, generated by implantation of oxygen and zinc ions into ZnO thin films, have now been started by us [40]. The pulsed laser deposition (PLD) technique on a-plane sapphire substrates [41] was employed for the growth of c-plane oriented ZnO films of ~ 1 \( \mu m \) thickness. Ion implantation was carried out with oxygen at four different energies (30, 70, 120, and 200 keV) to obtain a ~ 400 nm box-like implanted region with an additional oxygen concentration of ~ 1 \( \times \) \( 10^{17} \) \( \text{cm}^{-3} \) (as calculated by SRIM [42]). The zinc implantation was carried out with a single energy of 250 keV to a fluence of 5 \( \times \) \( 10^{11} \) \( \text{cm}^{-2} \).

Thermal annealing has been employed to reduce the density of implantation-induced defects in the film samples. In preparation for capacitance spectroscopic measurements Schottky contacts, realised by thermally evaporating Pd, have been deposited onto the samples. To obtain the energetic depth and concentration of electrically chargeable traps present in the film samples, DLTS and Thermal Admittance Spectroscopy (TAS) measurements at the implanted as well as reference samples have been performed.

These experiments are suitable for the investigation of electronic states having thermal activation energies in the range from several meV up to 1 eV below the conduction band edge. Furthermore, they allow a distinction between defects that preferentially form under either oxygen or zinc rich conditions. Such measurements finally revealed that oxygen implantation generated a ~170 meV deep trap (yet unlabeled), and the well-known E4 [43] trap. After the Zn implantation and thermal annealing of the film sample, no new defect species could be detected but the concentration of a (yet unlabeled) ~210 meV deep trap was observed to increase.

2.2. Variation of growth conditions

2.2.1. ZnO nanostructures. Compared to thin film samples, \( p \)-type doping of ZnO nanostructures has been less comprehensively studied. Doping of ZnO nanostructures with acceptor impurities during growth [44-46], as well as by post-growth treatment [47-49] has been demonstrated. However, the doped nanostructures are usually characterized mainly in terms of their structural and optical properties, while characterization of electronic properties and confirmation of \( p \)-type conductivity is rarely performed, mainly due to experimental difficulties in electronic characterization of single nanostructures.

Examples of incorporation of acceptor impurities by post-fabrication treatment include nitrogen doping by calcination of ZnO nanoparticles in ammonia [47], as well as annealing of nanorods grown on a GaAs substrate, which results in diffusion of As acceptors into the nanorods [48]. \( p-n \) homojunctions have been fabricated by achieving \( p \)-type doping of HTG ZnO nanorods by exposure to a NH\(_3\) plasma [49].
Concerning doping during growth, one of the major difficulties is the change of the morphology of ZnO nanostructures with addition of the dopant [46]. Nevertheless, there have been several examples of successful doping of ZnO nanowires with an acceptor dopant introduced during growth [44, 45]. Phosphorus doped ZnO nanowire arrays have been fabricated by the CVD method using P2O5 as a dopant source [45]. As-grown nanowires exhibited n-type conductivity, while p-type conductivity was obtained after annealing in nitrogen at 850 ºC [45]. P2O5 was also used as a dopant for the fabrication of P:ZnO nanowires using PLD [44].

Doped ZnO nanostructures can also be prepared by chemical methods, where the dopant is introduced into the solution during synthesis of the nanostructures [50]. P-type and n-type ZnO nanoparticles have been prepared using this approach, and a rectifying behavior was observed in the junctions consisting of a p-ZnO nanoparticle layer and an n-ZnO nanoparticle layer [50].

In addition to the p-type behavior observed in samples with intentionally incorporated acceptor impurities, p-type behavior in undoped ZnO nanorods grown by a HTG method [51] has recently been observed. A scanning electron microscopy (SEM) image of the undoped p-type ZnO nanorods is shown in figure 2. The p-type behavior was attributed to an increased concentration of VZn and a decreased incorporation of donor impurities [51]. The type of conductivity was strongly dependent on the type of seed layer used for the nanorod growth [51]. In addition, the growth of nanorods on ITO substrates was found to be detrimental for the achievement of p-type conductivity due to diffusion of indium during seed/nanorod fabrication [51]. This illustrates the importance of native defects in the achievement of p-type conductivity in ZnO.

Defects in HTG nanorods are typically abundant due to a very low growth temperature (90 ºC). However, a large variation in sample properties can be achieved by changing the fabrication conditions and/or post-fabrication processing. An ambipolar behavior of field effect transistors (FET’s) based on HTG ZnO nanorods has also been attributed to native defects [52]. Measured electron and hole mobilities in these samples were comparable (3.2 and 2.1 cm²V⁻¹s⁻¹, respectively) [52].

2.2.2. ZnO thin films. p-type behavior has been observed in ZnO films prepared by different methods [5, 53-57]. Nitrogen doped ZnO grown by laser molecular beam epitaxy (MBE) has been reported and
a homojunction light emitting diode (LED) has been demonstrated [5]. The crucial part in obtaining these devices was a careful optimization of the growth conditions [5]. MOCVD grown homo-junction ZnO LED’s have also been demonstrated, although in this case for the achievement of p-type conductivity annealing in a N₂O plasma was necessary in addition to the introduction of a N dopant during growth from an ammonia source [53]. Homojunction devices based on other dopants have also been demonstrated, such as p-ZnO:Sb/n-ZnO:GaN junction grown by MBE [54].

In addition to doping with a single acceptor, co-doping for achieving p-type ZnO has also been investigated [55-57]. Co-doping with both acceptor and donor impurities [55, 56] and with two acceptor impurities [57] has been demonstrated. (Al, As):ZnO [55] and (Cu, Ga):ZnO [56] films were fabricated by radio frequency (rf) magnetron sputtering, while (Li, N):ZnO films were prepared by PLD [57].

Thus, the doped ZnO films can be prepared by a variety of experimental techniques. Key issues in achieving p-type doping are an optimization of the growth conditions and a good control over native defects to avoid compensation effects. In addition, for some acceptor impurities p-type conductivity can be attributed to the formation of complexes with native defects. For example, for the As impurity it has been proposed that the actual acceptor is an AsZn–2VZn complex, rather than an arsenic antisite (AsO) [34, 55].

Only recently, As-doped ZnO films were grown by the rf magnetron sputtering method [58]. As the substrate temperature during growth was raised above ~ 400 °C, the films changed from n-type to p-type. A hole concentration and mobility of ~ 6 × 10¹⁷ cm⁻³ and ~ 6 cm² V⁻¹ s⁻¹, respectively, were achieved. The ZnO films were studied by SIMS, X-ray photoelectron spectroscopy (XPS), low temperature photoluminescence (PL), and PAS. The results were found to be consistent with the AsZn–2VZn shallow acceptor model proposed by Limpijumnong et al. [34]. The results of XPS, PL, PAS, and thermal studies finally allowed suggestion of a comprehensive picture of the As-related shallow acceptor formation.

The importance of native defects in the achievement of p-type conductivity in ZnO is also confirmed by recent reports of p-type conductivity in undoped ZnO films, which was attributed to VZn acceptors [59] or complexes consisting of VZn and another acceptor [60]. Thus, while p-type behavior can be achieved by varying the growth conditions of ZnO for a certain number of dopants, and even in the absence of dopants, further work is still needed to achieve a full understanding of the relevant phenomena and stable and reproducible p-type doping.

2.3. Issue of Schottky contacts

Developing the techniques for fabricating good quality Ohmic and Schottky contacts on ZnO is an essential step for device fabrication. Ohmic contact fabrication is relatively easy, but the relevant knowledge in fabricating a Schottky contact on ZnO is not thoroughly understood. According to the Schottky-Mott model, the barrier height of an ideal Schottky contact φb is given by the difference between the metal work function φm and the semiconductor electron affinity χ, i.e., φb = φm − χ. Thus, any metal having a work function larger than the electron affinity of ZnO (4.35 eV [61]) would be a candidate for forming a Schottky contact. The Schottky barrier height increases with the value of the metal work function. This implies that metals like Pt (φ = 5.65 eV), Pd (φ = 5.12 eV) and Au (φ = 5.10 eV) [62] would form a Schottky contact with the calculated Schottky barrier equal to 1.30 eV, 0.77 eV, and 0.75 eV, respectively. However in practice, depositing these metals onto an untreated ZnO surface usually results in a contact which is Ohmic in nature.

In practice, the electrical property of the fabricated Schottky contact also depends on other factors such as surface contamination, Fermi level pinning, chemical reaction at the interface, surface morphology, etc. [3, 20].

There is some literature reporting the fabrication of good quality Schottky contacts using the metals Au [63-70], Ag [67, 71], Pt [72-74] and Pd [63, 64, 75, 76]. Most of these successful cases involved surface pre-treatments, like wet etching (H₂O₂ [73, 77-79] and sulphide [74]), ozone treatment [72] and plasma cleaning [65, 70].
With the aim to explore the mechanisms that determine the contact electrical properties, efforts have also been devoted to study the correlations between the contact’s electrical properties and the surface conditions (like contamination, interfacial defects, interfacial layer morphology, etc.) with different pre-treatments. However, the problem was not unambiguously understood. The improvement of the contact rectifying property has been associated by different authors with a good surface morphology, the removal of deep level defects [73, 80], the formation of a low conductivity layer [69, 73, 76-78], and the removal of OH and C contaminations [70, 72, 77-79].

2.4. Incorporation of H and N into structural defects
A full chemical analysis of each material is essential for two reasons: (i) to determine the detailed content of any impurities and their corresponding concentrations, and (ii) to compare the values with the sensitivity limits of PAS. In a previous study [13] of various, nominally undoped, HTG and MG ZnO single crystals chemical compositions have generally been estimated by ICP-MS using a Perkin-Elmer ELAN-9000 spectrometer.

To account for the possible influence of hydrogen on the properties of ZnO – as there is an ongoing debate in the literature – an experimental estimation of the real H content of each crystal has been performed by NRA [13] also using 6.64 MeV $^{15}$N ions, as successfully demonstrated earlier for HTG ZnO nanorods [81]. NRA has a depth resolution of $\sim$ 5 nm, and the hydrogen detection limit is $\sim$200 ppm. The depth chosen for the analysis is estimated by SRIM calculations [42].

From SRIM it is also found that the analyzing $^{15}$N ions lose their kinetic energy $E$ with increasing penetration depth $x$ mainly by electronic stopping ($\left(\frac{dE}{dx}\right)_{\text{electronic}} = 2.52$ keV nm$^{-1}$), whereas nuclear stopping is about three orders of magnitude smaller ($\left(\frac{dE}{dx}\right)_{\text{nuclear}} = 0.006$ keV nm$^{-1}$). This energy transfer to the crystal during analysis can be sufficient to release a weakly bound hydrogen atom from its bonding site, so that it will be able to start diffusion. It is generally assumed that single H atoms would be trapped again immediately so that this diffusion should most probably take place in the form of H$_2$ molecules. As this diffusing hydrogen is then no longer available at the analysis position, this is seen as a drop in concentration with increasing $^{15}$N fluence. Throughout this paper we will call this “unbound H (H-u)”. All H atoms which are not moving during analysis because the energy transfer is not sufficient to release them from their bonding site will be called “bound H (H-b)”. However, it has to be clearly stated also that from NRA it is impossible to draw any conclusion on the kind of bonding of H atoms in the crystal.

It has been found that H-b exists in all crystals with a high concentration (at least 0.3 at.-%). On the other hand, saturated positron trapping has generally been observed in the crystals known to occur usually for vacancy-like defect concentrations $> 0.01$ at.-% [9]. However, all non-hydrogen impurities detected were found to have their concentrations apparently below this limit and thus can hardly influence the positron lifetime data even if they would form a complex with vacancies. NRA results further have led to the conclusion that H-u has no influence upon the positron lifetimes observed. From the comparison of theoretical calculations with the experimental results it has been concluded that most probably a ($V_{\text{Zn}} + 1\text{H}$) complex could account for the positron lifetime observed in HTG crystals. However, a ($V_{\text{Zn}} + 2\text{H}$) complex has been estimated to be unable to trap a positron, and thus the explanation of the positron lifetime generally observed in MG crystals (165-167 ps) remained unexplained [13].

To account for the possible influence of nitrogen on measurable positron properties, its concentration had to be determined. To estimate and compare the total N content of an HTG (MT-08) and an MG (B12) ZnO single crystal, a “multi N/C 2100S” device from Analytik Jena AG has been used.

The corresponding sample of a given weight is dissolved in 1ml of 30% HCl (suprapure quality) and diluted to 10 ml with Milli-Q-water®, then an amount of 500 µl is injected into an oven, where by use of a Pt catalyst in a stream of oxygen gas the dissolved sample is converted into NO$_X$. The amount of NO$_X$ is determined by a well calibrated chemo-luminescence detector. Routinely this is done for samples having a nitrogen content of the order mg/l. The detection limit of the commercial device is
given to be 100 μg/l. Our HTG sample (MT-08) had a total weight of 0.241 g, whereas the MG sample (B12) had a total weight of 0.0839 g only. No nitrogen has been detected in both samples, i.e. the nitrogen content should be <4 μg/g for sample MT-08 and <12 μg/g for sample B12. These values of an upper limit of the nitrogen content can be expressed also as 11.6 ppm \((9.6 \times 10^{17} \text{ cm}^{-3})\) for the HTG (MT-08) sample and 34.9 ppm \((29.3 \times 10^{17} \text{ cm}^{-3})\) for the MG sample (B12), respectively.

On the other hand, these estimated upper limits of the nitrogen content should be related with the experimentally determined concentration of H-b = \((0.14 \pm 0.03)\) at.-\% \((1400 \text{ ppm})\) and \((0.40 \pm 0.03)\) at.-\% \((4000 \text{ ppm})\) for the HTG and MG samples, respectively, where on the other hand no indication of the presence of H-u could be seen from NRA in both crystals. Thus, a ratio of H:N = 121 for the HTG sample (MT-08) and H:N = 115 for the MG sample (B12) can be estimated. These ratios are almost equal for both investigated samples, which had to be expected because for their evaluation the estimated upper limits of the given method for both crystals have been used. Thus, a ratio H:N ~ 120 should represent a lower limit for the HTG and MG ZnO crystals investigated here because the real nitrogen concentration in both types of samples should be less (and absolute concentrations remain to be determined by a more sensitive method in the future).

Nevertheless, the given results allow one to draw two major conclusions so far: (1) H again turns out to be the impurity with the highest concentration in both types of crystals, compared to other detected impurities and to nitrogen, which has not yet been really detected [13], and (2) taking the estimated upper limits of the nitrogen concentration to represent the real content would mean that N-related open volume defects could play a role in the variety of conceivable structural defects which are able to trap positrons and thus influence the measurable positron lifetime spectrum. The latter conclusion challenges and justifies the calculation of positron properties of such defects, and the results of first calculations are presented and discussed in the next chapter.

3. Theory

3.1. Brief description of calculations

In order to understand the structure of defects related to N and H impurities, we have performed ab initio studies of such defects aiming mainly at the defects’ structure and their positron characteristics. For this purpose we employ the Vienna ab initio package (VASP) [82] considering projected augmented wave potentials [83] in order to get relaxed defect geometries. Positron calculations have been performed using a real space method as implemented in the atomic superposition method (ATSUP) [84]. More details regarding calculations can be found in our recent work [13].

![Figure 3. Perfect ZnO lattice (hexagonal, wurtzite) together with a ZnO₄ tetrahedron. Red (blue) spheres mark O (Zn) atoms.](image-url)
3.2. Summary of results for H-related defects

Hydrogen can be incorporated into the ZnO lattice in several ways [85]. First, these are ‘bond-center’ positions in which H atoms are located approximately in the middle of the original Zn-O bonds (inside the corresponding \( \text{ZnO}_4 \) tetrahedron; see figure 3), which causes a substantial lattice distortion at the position of defects. Second, there also exist ‘antibonding’ positions where the H bond is located outside \( \text{ZnO}_4 \) tetrahedra. Furthermore, hydrogen atoms may occupy vacancies on both Zn and O sublattices as suggested in [39, 86]. In addition, weakly bound H atoms (in the form of \( \text{H}_2 \) molecules) may reside in ‘channels’ (along the hexagonal axis) in the ZnO structure [85]. Hydrogen atoms can also be bound to other impurities.

As for hydrogen incorporated in single vacancies, it was found that the H atom resides in the center of an oxygen vacancy. Bonding properties of H in such a defect is a matter of ongoing discussion [39, 87], but positrons do not trap in such a defect [11, 87]. Concerning the Zn vacancy \( V_{\text{Zn}} \), incorporation of one, two and three H atoms has been studied [13]. Like interstitial H in the ZnO lattice [85], H atoms make a bond inside \( V_{\text{Zn}} \) with a neighboring oxygen atom with a bonding length of about 1 Å. The hydrogen molecule is not stable inside \( V_{\text{Zn}} \). The details of configurations are given in Ref. [13]. Here we point out that with the increasing number of H atoms inside the vacancy the open volume available for positron trapping (and the depth of the positron potential well) is decreasing and already the \( V_{\text{Zn}} + 2 \text{H} \) complex does not trap positrons. In the case of the \( V_{\text{Zn}} + 1 \text{H} \) complex, positrons can be trapped and, depending on the configuration, the positron lifetime ranges from 177 to 179 ps (considering positron induced forces). Such lifetimes are very close to those measured for HTG samples and it was therefore suggested that the \( V_{\text{Zn}} + 1 \text{H} \) complex is responsible for saturated trapping in HTG samples, though other defect configurations need to be yet investigated to prove this suggestion. In particular, the investigation of the zinc plus oxygen (\( \text{Zn} + \text{O} \)) di-vacancy containing a varying number of hydrogen atoms is in progress.

3.3. First calculations for N-vacancy complexes

We present here the first results of investigations of charge neutral \( V_{\text{Zn}} + 1 \text{N} \) and \( V_{\text{Zn}} + 2 \text{N} \) complexes that could possibly trap positrons and thereby would become detectable by PAS. The structure of the studied defects is shown in figure 4. In positron calculations we restricted ourselves to the superposition of atomic densities and potentials, neglecting thus charge transfer effects and positron induced forces.

\[ \text{Figure 4. Atomic configurations of a) } V_{\text{Zn}} + 1 \text{N and b) } V_{\text{Zn}} + 2 \text{N defects studied. The color designation is the same as in figure 3 and yellow spheres mark nitrogen atoms. Thick lines indicate the original (undistorted) } \text{VO}_4 \text{ tetrahedron.} \]
The $V_{Zn} + 1N$ defect (figure 4a) was obtained using the starting configuration in which the N atom was placed into the same position where the hydrogen atom resides. After relaxation the N atom moves from the starting position and is bound to two neighboring O atoms (bond length ~1.4 Å, O-N-O bond angle ~111º). Thereby the original $VO_4$ tetrahedron becomes substantially distorted. The positron lifetime calculated for such a defect amounts to 166 ps, which indicates weak positron trapping. This could be eventually changed into a non-trapping defect after considering charge transfer effects and positron induced forces, but such calculations are not straightforward and still need to be performed.

As for the $V_{Zn} + 2N$ defect (figure 4b), there is an O-N-N-O chain of atoms with the O-N (N-N) bond length about ~1.45 Å (~1.25 Å); N-N-O bond angle is about 127º. Again the original $VO_4$ tetrahedron is found to be largely distorted. The corresponding positron lifetime is 159 ps and indicates no positron trapping as this value has also been obtained for the defect-free bulk of ZnO [11]. We note that N-O (N-N) bond lengths given above are somewhat longer (by about 10%) than those for NO/NO$_2$ (N$_2$) free molecules, which contrasts with the O-H bond length that is always very close to 1 Å, as in the H$_2$O free molecule. We may finally state that if $V_{Zn}$-nitrogen complexes do represent positron traps then they will be very shallow, though other possible configurations need to be further investigated.

4. Conclusions

Although the intrinsic properties of ZnO provide significant advantages for a variety of device applications, the reliable formation of $p$-type conductivity still remains a challenging goal. In particular, in this work the potential role of PAS to help identification of open volume defects that might be involved is mentioned.

First, efforts to achieve $p$-type conductivity of ZnO by ion implantation are reviewed, and the creation of a $p$-$n$ junction by N$^+$ ion implantation and thermal annealing is discussed. Second, ways to achieve $p$-type ZnO of thin films and nanorods by various growth conditions are summarized. A very recent example of achieving finally $p$-type ZnO:As by radio frequency magnetron sputtering at elevated temperature is given. This result was found to be consistent with the As$_{Zn}$ – $2V_{Zn}$ shallow acceptor model proposed theoretically by Limpijumnong et al. [34].

Third, the preparation of Schottky contacts on ZnO is mentioned in some detail as this also makes serious demands of any device formation process.

Finally, the possible incorporation of hydrogen and nitrogen into structural defects, which can act as trapping sites for positrons, is considered. The $V_{Zn} + 1$ H complex has been found to trap a positron, whereas the $V_{Zn} + 2$ H complex does no longer constitute such a trap [13]. Correspondingly, first calculations by ATSUP reveal that the $V_{Zn} + 1$ N complex is just a weak positron trap, whereas the $V_{Zn} + 2$ N complex does not constitute such trap at all. As a ratio H:N ~ 120 is determined to be a lower limit for the HTG and MG ZnO single crystals investigated here, there is a marginal influence expected of the N-related complexes considered so far on measurable positron lifetime spectra. The probability to detect the $V_{Zn} + 1$ N complex experimentally by PAS is very low in any case.

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