Lattice location of the group V elements As and Sb in ZnO

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Abstract

The lattice locations of the potential *p*-type dopants arsenic and antimony in single-crystalline ZnO were studied by means of the electron emission channeling method following the implantation of radioactive ⁷³As and ¹²⁴Sb isotopes. The majority of the implanted As and Sb probe atoms was found to occupy substitutional Zn sites, with the possible fraction on substitutional O sites being at maximum a few percent. The obtained results illustrate the difficulty in introducing oversized group V impurities on O sites and thus put further into question whether these elements may act as simple chemical dopants in ZnO. © 2009 Elsevier Science. All rights reserved

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1. Introduction

Modifying the electrical properties of ZnO by means of incorporating nitrogen, phosphorus, arsenic or antimony impurities is of interest since these group V elements have been reported in the literature among the few *p*-type dopants in this technologically promising II-VI compound [1]. While there is little doubt that the relatively small N³⁻ ion (ionic radius 1.46 Å) replaces an O²⁻ anion (1.38 Å), acting as a singly ionized acceptor, the large size mismatch between O²⁻ and the potential acceptor ions P³⁻ (2.12 Å), As³⁻ (2.22 Å) or Sb³⁻ (2.45 Å) makes the simple substitution of O²⁻ anions unlikely [2]. On the other hand, the much smaller radii of the triply positive ions P³⁺ (0.44 Å), As³⁺ (0.58 Å) or Sb³⁺ (0.76 Å) should favour the substitution of Zn²⁺ (0.60 Å) cations, resulting in donor

formation. With respect to ionic size, another possibility seems to be the replacement of O²⁻ by neutral As⁰ or Sb⁰. The radii of the corresponding ions in various configurations are illustrated in Fig. 1 using simple ball models. Reaching beyond simple size and stability arguments, density functional theory suggests that P_O, As_O or Sb_O (i.e. replacing oxygen) act as deep centers and not as shallow acceptors [3,4], while the *p*-type behaviour was attributed to the formation of electrically active acceptor complexes of the type As_{Zn}-2V_{Zn} or Sb_{Zn}-2V_{Zn} [4,5]. However, it is still strongly disputed in the literature whether the experimentally observed *p*-type character in ZnO is due to P, As or Sb simply replacing oxygen (cf. Ref. [6,7]) or to the formation of more complicated defects.

In order to understand the mechanism of *p*-type doping in ZnO, experiments that reveal the lattice location of group V impurities are crucial. We have previously determined the lattice sites of ion implanted As in ZnO by means of

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FIG. 1. (Color online) Ball models illustrating the ionic sizes of Zn, O, As and Sb for various configurations in zinc oxide. (a): In the undisturbed ZnO lattice, the bond length $b = 1.953 \text{ \AA}$ between neighboring Zn and O atoms almost exactly matches the sum of the ionic radii of Zn^{2+} ($0.60 \text{ \AA}$) and O^{2-} ($1.38 \text{ \AA}$) due to the comparatively strong ionic character of the bonds. The leftmost Zn^{2+} ion has been replaced with an As^{3+} ion of radius $0.58 \text{ \AA}$ in (b) and with an Sb^{3+} ion of $0.74 \text{ \AA}$ in (c), illustrating the good size match between As^{3+} or Sb^{3+} and Zn^{2+} . Panels (d) and (e) illustrate that As^{3+} or Sb^{3+} ions with their large radii of $2.22 \text{ \AA}$ and $2.45 \text{ \AA}$, respectively, do not fit within the cage of the surrounding four Zn^{2+} ions. In contrast, neutral As^0 (f) or Sb^0 (g) atoms with their covalent radii of $1.20 \text{ \AA}$ or $1.40 \text{ \AA}$ would fit within the cage of the surrounding four Zn^{2+} ions.

conversion electron emission channeling from radioactive ^{73}As ($t_{1/2}=80.3 \text{ d}$) [8-10]. In this contribution we present new data on β^- emission channeling experiments using the implanted radioactive isotope ^{124}Sb (60.2 d) and compare the behaviour of the two dopants.

2. Experimental

Radioactive ^{73}As and ^{124}Sb isotopes were produced and ion implanted into two single-crystalline c-axis oriented ZnO samples using the ISOLDE facility at CERN. The chosen implantation conditions were a fluence of $2 \times 10^{13} \text{ cm}^{-2}$ with 60 keV energy for ^{73}As and $1 \times 10^{14} \text{ cm}^{-2}$ with 30 keV for ^{124}Sb , both at angles of $7\text{-}10^\circ$ with respect to the surface normal. While the sample implanted with ^{124}Sb was hydrothermally grown and obtained from CrysTec GmbH, the sample used for the ^{73}As implantation was a SCVT-grown crystal purchased from Eagle Picher Technologies. The angular distributions of the emission of $42\text{-}52 \text{ keV}$ conversion electrons resulting from the decay of ^{73}As and of β^- particles from the decay of ^{124}Sb (endpoint energy 2.30 MeV) were measured using a position-sensitive Si pad detector [11] within an angular range of $\pm 2.6^\circ$ around the crystallographic directions $[0001]$, $[-1102]$, $[-1101]$, and $[-2113]$. The measurements were done in the room-temperature as-implanted state and following several 10-min annealing steps up to 900°C under vacuum better than 10^{-5} mbar . In order to

quantitatively characterize the lattice sites of the emitter atoms, the emission channeling patterns were fitted by theoretical patterns corresponding to a combination of up to three different high-symmetry lattice positions. The theoretical emission yields for a variety of possible lattice sites were calculated using the “manybeam” formalism [12]. More information on the details of the experimental conditions and the theoretical calculations have been published previously [8-11,13].

3. Results and discussion

Figure 2 (a)-(d) shows the angular-dependent emission yield of β^- particles from ^{124}Sb as measured in the as-implanted state around the four crystallographic directions of ZnO mentioned above. The fact that prominent channeling effects are observed for all four axial directions and for the major planes can only be explained by a large fraction of emitter atoms on substitutional sites. The best fits of theoretical patterns to the experimental data that allow for a fraction of emitter atoms on only one highly symmetric lattice site with the remainder on random sites, are shown in Fig. 2 (e)-(h). They were obtained for 58% of ^{124}Sb emitter atoms aligned with the c-axis, and 47%, 51% and 57% at substitutional S_{Zn} sites. The root mean square (rms) displacements perpendicular to the corresponding channeling directions, $u_1(^{124}\text{Sb})$, which gave the best fits were $0.11 \text{ \AA}$, $0.08 \text{ \AA}$, $0.13 \text{ \AA}$, and $0.16 \text{ \AA}$. Note that, as has been previously pointed out, emission channeling patterns resulting from emitter atoms on other lattice sites, e.g. substitutional S_{O} or interstitial T sites, are distinctively different from the S_{Zn} site patterns and typical examples for such calculated patterns have been shown in Refs. [8,13].

In order to assess the possible fractions of ^{124}Sb emitter atoms on substitutional S_{O} sites and interstitial T sites, three-site fits were carried out, where, apart from random sites, fractions of emitter atoms on S_{Zn} , S_{O} and T sites were simultaneously allowed in the fits. In addition, the rms displacement of the fraction of ^{124}Sb on S_{Zn} sites was optimized. The results as a function of annealing temperature are compiled in Fig. 3 (a)-(b). As can be seen, the fitted fractions on S_{O} and T sites are at maximum 5-6%. However, such small fractions are at the detection limit of the technique, which is illustrated by the fact that the fraction on S_{O} sites becomes a few percent negative following $T_{\text{A}}=900^\circ\text{C}$, which is of course not physically possible but the result of statistical uncertainty in the fitting procedure. It is hence doubtful whether any ^{124}Sb emitter atoms actually occupy the S_{O} or T sites. The rms displacements for Sb on S_{Zn} sites as derived from the best fit results, are on average somewhat larger but close to those reported in the literature for Zn atoms at room temperature, $u_1(\text{Zn})=0.078\text{-}0.097 \text{ \AA}$ [14-16]. Only following annealing at 900°C the rms displacements of ^{124}Sb are clearly above those values.

FIG. 2. (Color online) Angular distribution of normalized β^- emission yields from ^{124}Sb in ZnO in the as-implanted state around the (a) [0001], (b) [-1102], (c) [-1101] and (d) [-2113] axis. (e)-(h): Best fits of the channeling patterns corresponding to 58% of ^{124}Sb aligned with the c-axis, and 47%, 51% and 57% at substitutional S_{Zn} sites, respectively. The blue regions at the edge of the theoretical patterns are outside the range of $\pm 3^\circ$ from the axes for which the theoretical yield was calculated.

Comparing the lattice location results for ^{124}Sb to those obtained previously for ^{73}As [Fig. 3 (c)-(d)], both elements obviously have in common that the majority of probe atoms occupy the S_{Zn} sites while the fraction on S_{O} sites is at maximum a few percent for all annealing temperatures. Moreover, in both cases the impurity rms displacements from the ideal S_{Zn} sites are within a factor of two of the Zn rms displacements. The rms displacements $u_1(^{73}\text{As})$ tend to show greater scatter. While this could in principle be due to static displacements or anisotropic thermal vibrations of As, the relatively low energy of the ^{73}As conversion electrons (42-52 keV) makes them subject to more pronounced dechanneling, which causes a higher uncertainty in deriving u_1 .

Besides the mentioned similarities of Sb and As, however, two differences are also obvious. Firstly, in contrast to ^{73}As , the probe atom ^{124}Sb shows higher

FIG. 3. (Color online) Fractions of ^{124}Sb (a) and ^{73}As (c) on substitutional Zn (S_{Zn}), substitutional O (S_{O}), interstitial T, and random sites as obtained from three-site fits as a function of annealing temperature. The best fit values for the rms displacements of the ^{124}Sb (b) and ^{73}As (d) emitter atoms from ideal S_{Zn} sites, perpendicular to the four measured crystallographic directions, and derived from the same type of fitting procedure. The two dotted lines indicate the range of room temperature rms displacement values of Zn atoms reported in the literature.

fractions on random sites; in particular already for annealing temperatures up to 600°C the random fraction found is 30-40%. This could be a consequence of the implantation conditions for this sample ($1 \times 10^{14} \text{ cm}^{-2}$ of mass 124 at 30 keV vs $2 \times 10^{13} \text{ cm}^{-2}$ of mass 73 at 60 keV) which result in a higher amount of lattice damage. However, we believe that this is to some extent also an artifact of the background correction procedure for the ^{124}Sb isotope. Since electrons have high cross sections for scattering, electron emission channeling experiments always require a correction for electrons which are backscattered from the sample and the walls of the vacuum setup into the detector. For conversion electron emitters such as ^{73}As the amount of elastically backscattered electrons can be corrected quite accurately by extrapolating the amount of inelastically scattered electrons at lower energies into a trapezoidal background that is subtracted from the conversion electron lines. For β^- emitters such a procedure is not possible due to the continuous nature of the β^- spectra. In this case the background correction relies on Monte Carlo electron scattering simulations using the GEANT4 code [17], assuming an isotropic source with an electron energy distribution resulting from the β^- spectrum of ^{124}Sb and taking into account the elemental composition and geometrical features of the sample, the sample holder, the vacuum setup, and the detector. The experimental patterns for ^{124}Sb were corrected by subtracting an isotropic background contribution of 49%, and any underestimation of this value results in an increase of the random fraction determined in the fit.

Secondly, for annealing temperatures above 600°C, the fraction of ^{124}Sb on S_{Zn} sites decreases continuously, accompanied by an increase of the random fraction. The decrease of the S_{Zn} fraction is less pronounced for ^{73}As and, moreover, is unambiguously accompanied by the increasing occupation of interstitial T sites. It has been recently described in the literature that the annealing of ZnO above 600°C causes the loss of O from depths up to 100 Å even when it is carried out under O_2 atmosphere [18]. Such a loss of O should be even more pronounced for our annealing conditions under vacuum, and it seems probable that it introduces O vacancies in the neighbourhood of the probe atoms. On the other hand, the onset of Sb diffusion in ZnO is likely to occur around 800°C [19]. If Sb atoms are able to migrate, they may either pair with other defects resulting from the implantation process or the vacuum annealing (e.g. O vacancies) and thus be incorporated on random sites, or the implantation profile may substantially change, resulting in an increase of dechanneled electrons. In order to investigate the possible influence of the annealing atmosphere, experiments are currently under way which study the lattice location of ^{73}As in ZnO samples annealed in air.

Finally we would like to mention that we have recently undertaken first exploratory β^- emission channeling experiments using commercially available ^{33}P (25.3 d) which was implanted into ZnO using the ion implanter at IKS Leuven. Although the implantations suffered from a so far unidentified contamination of a stable isotope, the preliminary analysis showed that also phosphorus prefers substitutional S_{Zn} sites in ZnO.

4. Conclusions

We find, in contrast to what one might expect from their nature as group V elements, that both As and Sb do *not* occupy substitutional S_{O} sites in ZnO but mostly substitutional S_{Zn} sites. Possible fractions of As or Sb on O sites in our experiments, if existing at all, could at maximum have been a few percent. Arsenic and antimony in ZnO are thus interesting examples for impurities where the *major* impurity lattice site is determined by ionic size rather than their position in the periodic system. While our results cannot settle the interesting issue whether substitutional As or Sb on oxygen sites or $\text{As}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ or $\text{Sb}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ complexes are responsible for the acceptor action, the fact that implanted As and Sb prefer the substitutional S_{Zn} sites is clearly a strong argument in favour of the complex acceptor model, while it discourages the notion that As and Sb act as simple “chemical” acceptors in ZnO.

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