Direct evidence for Sb as a Zn site impurity in ZnO

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The lattice location of ion implanted antimony in zinc oxide has been determined by means of β− emission channeling from the radioactive 124Sb isotope. Following 30 keV implantation of 124Sb into a single-crystalline ZnO sample to a fluence of 1×1014 cm−2, the angular-dependent emission rate of β− particles around several crystallographic directions was measured with a position-sensitive Si detector. The majority of Sb was found to occupy Zn sites, with the possible fraction on O sites being at maximum 5-6%. © 2009 American Institute of Physics. [DOI: 10.1234/1.1234567]

To date, the group V element antimony is one of the elements which have been used as p-type dopants in the II-VI semiconductor zinc oxide, the others being N, P and As (cf. Ref. [1] and Refs. therein). In the case of Sb, following the report of Sb-doped p-type ZnO by Aoki et al in 2002 [2] and further work by other authors [3-6], recently the realization of a wide range of optoelectronic devices incorporating p-type ZnO:Sn layers have been reported, including homo- and heterojunction photodiodes [7-8], ultraviolet (UV) light emitting diodes (LEDs) [9-12], and UV lasers [13].

While technological applications of p-type ZnO seem thus to have come within reach, the nature of the acceptors in P, As or Sb-doped ZnO continues to be disputed in the literature. From a simple viewpoint of chemical bonding, the substitution or Sb-doped ZnO continues to be disputed in the literature. The production and implantation of 124Sb were performed available from CrysTec GmbH) into which 124Sb was implanted at room temperature with 30 keV energy to a fluence of 1×1014 cm−2. The Sb depth profile corresponding to these implantation conditions is centered at a depth of 106 Å, with a straggling of 41 Å. The isotope 124Sb decays by the emission of β− particles with an endpoint energy of 2.30 MeV into stable 124Te, the mean value of the β− energy being 378 keV. The angular emission patterns of the β− particles in the energy window above 35 keV were recorded around the [0001], [100], [110] and [2113] directions at room temperature by means of a position-sensitive Si detector [30], in the as-implanted state and following 10-min. annealing steps at 200°C, 600°C, 800°C, and 900°C under vacuum below 10−5 mbar. The angular resolution due to the size of the implanted spot on the sample and the position resolution of the detector was ~0.16° (standard deviation). The evaluation of the probe atom lattice location was performed by quantitatively comparing the experimental patterns with theoretical ones calculated for 124Sb on various different lattice sites, using the two-dimensional fit procedure outlined in Ref. [30]. In the fit procedure, we considered theoretical patterns resulting from emitter atoms at substitutional Zn (Szn) and substitutional O (Soo) sites with varying isotropic root mean square (rms) Gaussian displacements, the main interstitial sites T and O (cf. Ref. [25, 27]), and a diversity of interstitial sites resulting from displacements along or off the c-axis. The theoretical β− emission channeling patterns were calculated by means of the “ma-nybeam” theory of electron diffraction in single-crystals [28]. The continuous electron spectrum from the β− decay was approximated in the calculations by a histogram with stepwidths of 25 keV electron energy up to 800 keV, of 50 keV up to 1.4 MeV, and of 100 keV up to 2.3 MeV. The number of beams used was 16 up to 725 keV electron energy, 20 up to 950 keV and 24 at all higher energies. Details with respect to the structural properties of ZnO used in the simulations have been given previously [31]. The experimental patterns were corrected by subtracting an isotropic background contribution of 49% resulting from electrons that have been backscattered into the detector from inside the sample or by parts of the vacuum setup. This background contribution was estimated by means of Monte-Carlo simulations based on the GEANT4 code [32], taking into account the elemental composition and geometrical features of the sample, the sample holder, and the vacuum setup, as well as the electron energy distribution resulting from the β− spectrum of 124Sb.
The experimental β− emission patterns along the [0001], [1102], [1101] and [2113] directions, following 600°C vacuum annealing, are shown in Figs. 1 (a)-(d). The channeling effect due to 124Sb, which corresponds to 70% of 124Sb along the c-axis with positions centered within the c-axis atomic rows. Fitting this experimental pattern by allowing only for emitter atoms with positions centered within the c-axis rows and on random sites, resulted in the theoretical pattern shown in Fig. 1 (e), which corresponds to 70% of 124Sb along the c-axis with an rms displacement of $u_r^{124Sb} = 0.14$ Å perpendicular to this direction. Note that this does not yet allow distinguishing between a preference for $S_{Zn}$ and $S_O$ sites since both are aligned with the [0001] axis, along with a number of interstitial sites, e.g. the T sites. The site preference of Sb, becomes obvious when the [1102], [1101] and [2113] experimental patterns are fitted in a similar way, however, in this case only allowing for emitter atoms on substitutional Zn and random sites. The resulting best fit theoretical patterns are shown in Fig. 1 (f)-(h) and correspond to 54%, 61% and 64% at substitutional $S_{Zn}$ sites with perpendicular 124Sb rms displacements of 0.10 Å, 0.14 Å, and 0.19 Å, respectively.

The fit value for the fraction of Sb atoms aligned with the c-axis is ~6-10% larger than those for Sb on Zn sites. This could indicate that some Sb atoms are located on sites that are aligned with the c-axis but are different from $S_{Zn}$ sites, e.g. $S_O$ or T sites. In order to test this hypothesis, fits were carried out for the [1102], [1101] and [2113] patterns, allowing for additional fractions on $S_O$ or T sites. Note that for these directions emitter atoms on $S_O$ or T sites would produce channeling patterns (Fig. 2) that are distinctly different from $S_{Zn}$ site patterns. However, this resulted only in minor improvements in the quality of fit, with the additional 124Sb fractions on $S_O$, T or other sites being in the 5-6% range at maximum. Figure 3 (a) shows the fitted fractions of Sb emitter atoms as a function of annealing temperature when both $S_{Zn}$ and $S_O$ sites were allowed in the fit. The fitted fraction for Sb on oxygen sites is never larger than 5-6%, which is at the detection limit of the technique for this isotope (note that around half of the count rate resulted from scattered electrons). On the other hand, the fitted fraction of Sb on Zn sites is around 50-60% for annealing temperatures up to 600°C and then drops to 20% following 900°C vacuum annealing. The derived values for the rms displacements of 124Sb [Fig. 3 (b)] are generally somewhat larger but close to those for Zn atoms at room temperature, where reports in the literature vary between 0.078 Å and 0.097 Å. We interpret the decrease of the fraction of Sb on Zn sites following 900°C vacuum annealing to be a consequence of the onset of Sb migration. This interpretation is supported by the fact that experiments where the diffusion of implanted Sb in ZnO was studied by means of secondary ion mass spectroscopy (SIMS) [33] observed slight changes in the implanted profiles for annealing temperatures at 800°C or above. If Sb atoms are able to migrate, they may either pair with other defects resulting from the implantation process or from the vacuum annealing and thus be incorporated on random sites, or the implantation profile may substantially change, resulting in an increase of dechanneled electrons.

The lattice location of 124Sb is in many respects similar to our previous results on implanted 73As in ZnO [25-27], where we found 70-90% of As on $S_{Zn}$ sites with the fraction on $S_O$ sites being less than a few per cent. While the fraction of 73As on $S_O$ sites also decreased following 900°C vacuum annealing, it was possible to identify that ~30% of As was relocated...
to sites close to the interstitial T position. In comparison to $^{73}$As, the experiments with $^{124}$Sb could only be analyzed assuming a relatively high fraction (>40%) on random sites. However, we believe that this may be the consequence of an underestimation of the background correction resulting from the scattering of high-energy electrons. While the background correction for the $^{73}$As emitter relies on simulation results using the GEANT4 code, the measured conversion electron energy spectrum of $^{73}$As directly allows determining the amount of inelastically scattered electrons, which is a more reliable procedure.

Summarizing, our findings clearly establish the preference of Sb for Zn sites and show that the fraction of implanted Sb on oxygen sites is at maximum a few per cent. It is hence evident that this may be the consequence of an underestimation of the background correction resulting from the scattering of high-energy electrons. While the background correction for the $^{73}$As emitter relies on simulation results using the GEANT4 code, the measured conversion electron energy spectrum of $^{73}$As directly allows determining the amount of inelastically scattered electrons, which is a more reliable procedure.

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**FIG. 3.** (Color online) (a) Fractions of $^{124}$Sb on substitutional Zn ($S_{Zn}$) and possible fractions on substitutional O ($S_{O}$) sites as a function of annealing temperature. (b) The best fit values for the rms displacements of the $^{124}$Sb emitter atoms from ideal $S_{Zn}$ sites, perpendicular to the four measured crystallographic directions. The two dotted lines indicate the range of room temperature rms displacements of Zn atoms.