Lattice site and stability of implanted Ag in ZnO

E. Rita^{* a,b}, U. Wahl^{a,b}, A.M.L.Lopes^c, J.P.Araújo^d, J.G. Correia^{a,b}, E.Alves^{a,b}, J.C.Souares^b,
The ISOLDE Collaboration^e

^a *Instituto Tecnológico e Nuclear, Sacavém, Portugal*

^b *Centro de Física Nuclear da Universidade de Lisboa, Lisbon, Portugal*

^c *Departamento de Física da Universidade de Aveiro, Aveiro, Portugal*

^d *IFIMUP, University of Porto, Porto, Portugal*

^e *CERN, Geneva, Switzerland*

In this work we report on the lattice location of implanted Ag in ZnO single-crystals, evaluated by means of the emission channeling technique. Following 60 keV low dose ($2 \times 10^{13} \text{ cm}^{-2}$) ion implantation, the β^- emission patterns from ^{111}Ag were monitored with a position-sensitive detector as a function of annealing temperature up to 800°C in vacuum. Our experiments revealed that in the as-implanted state around 30% of the Ag atoms are substitutional at the Zn site with root mean square displacements around 0.17-0.28 Å. Though this fraction did not change with increasing annealing temperature, upon annealing at 600°C the root mean square displacement of Ag from the Zn site increased considerably, followed by partial outdiffusion during 800°C annealing.

Keywords: ZnO, Ag, Emission Channeling, Lattice Location

* Corresponding author: Tel. +351-21-9946084; fax: +351-21-9941525; e-mail: erita@itn.mces.pt

1. Introduction

The range of applications of the II-VI semiconductor ZnO, as with any other semiconductor, is strongly dependent on the possibility of incorporating the appropriate dopants in the appropriate lattice sites. In spite of the similarities and advantages relatively to GaN, possible applications for ZnO are currently limited by the difficulty of achieving p-type doping of this semiconductor, which as-grown is always n-type. Besides the presence of compensating native defects [1], in the case of possible group *I* acceptors such as Li, Na or K the non-incorporation in substitutional Zn sites would also explain such behaviour, as was suggested in Ref. [2]. Silver, as a group *Ib* element, could also act as an acceptor in ZnO, if incorporated on substitutional Zn sites. However, previous studies, where Ag-doped ZnO was investigated with respect to its application in varistors, suggested that Ag acts as an amphoteric dopant, existing both on substitutional Zn sites and in the interstitial form [3]. A recent study [4], which investigated Ag doped ZnO using the photodoping method, found that the incorporation of Ag also influenced the intensity of the green luminescence from ZnO.

In this work, the lattice location of the radioactive isotope ^{111}Ag implanted in ZnO single-crystals was investigated by means of the Emission Channeling (EC) technique [5], as a function of the annealing temperature. The ^{111}Ag atoms decay with 7.45 days half-life by β^- emission to the stable isotope ^{111}Cd . Depending on the lattice site of the emitter atoms, the emitted β^- particles may be guided by the crystal potential close to the rows of lattice atoms on their way out of the crystal, that is, the electrons may be channeled. Measuring the angular distributions of the emitted β^- particles with a position sensitive detector allows then the evaluation of the lattice location of the emitter atoms.

2. Experimental Details

In this study, room temperature implantation of the ^{111}Ag radioactive isotope, with 60 keV energy and up to a dose of $2 \times 10^{13} \text{ cm}^{-2}$, was performed on a commercially available ZnO [0001] single-crystal (Comment: here we should supply more details on the crystal: supplier, growth method, Zn face or O face). The implantation took place at the CERN/ISOLDE facility [6], where pure beams of radioactive elements are produced, providing a large variety of isotopes for EC. During the implantation, a 7° tilt angle from the crystal surface was applied in order to reduce channeling of the ^{111}Ag atoms and to achieve a well-defined depth profile. With these implantation parameters the projected range and straggling of the Ag atoms are 185 Å and 72 Å, respectively.

By means of a position sensitive detection system [5], the angular distributions of the β^- particles emitted from the ^{111}Ag radioactive decay were measured around the [0001], $[\bar{1}102]$, $[\bar{1}101]$ and $[\bar{2}113]$ directions of the ZnO single-crystal, in order to achieve unambiguous information about the lattice site of the emitter. These measurements were performed in the as-implanted state and following 10 min *in situ* vacuum annealing steps at 200°C, 400°C, 600°C, and 800°C. For extraction of the emission channeling patterns, an energy window was set from 25 keV up to the β^- endpoint energy of 1.03 MeV.

The Ag lattice site location was subsequently evaluated by comparing the experimental emission channeling patterns with theoretical ones by means of the two-dimensional fitting procedure outlined in Ref [5]. The considered lattice sites were substitutional Zn sites (S_{Zn}) and substitutional O sites (S_{O}) with varying Gaussian root mean square (rms) displacements and a variety of interstitial sites, which are described in detail in Ref. [7]. The ^{111}Ag theoretical emission patterns were calculated by means of the “manybeam” theory of electron diffraction in single-crystals [8]. As described previously in Ref. [9], two models for the

wurtzite crystal structure of ZnO were considered, differing somewhat in the rms displacements of Zn and O atoms and the c -axis bond length parameter. Both models lead essentially to the same results for the ^{111}Ag lattice location.

3. Results and discussion

The experimental emission channeling patterns along the $[0001]$, $[\bar{1}102]$, $[\bar{1}101]$ and $[\bar{2}113]$ directions of ZnO, following the room temperature implantation of ^{111}Ag are presented in Fig.1 (a)-(d). The best fits of the theoretical patterns to the experimental ones are shown in Fig.1 (e)-(h) and they result from considering only two fractions for the Ag atoms, namely, ~30% substitutional at Zn sites (S_{Zn}) and ~70% at random sites. The best fit values of the Ag rms displacements from S_{Zn} sites were 0.18 Å, 0.17 Å, 0.20 Å and 0.28 Å perpendicular to the $[0001]$, $[\bar{1}102]$, $[\bar{1}101]$ and $[\bar{2}113]$ directions, which is larger than the thermal vibration amplitude of the Zn atoms of $u_1(\text{Zn}) = 0.082$ Å. Previous EC experiments performed on ZnO with ^{67}Cu [10], another group *Ib* element that could act as an acceptor in ZnO, yielded similar rms values in the as-implanted state. However, the fraction of Cu atoms at Zn sites was considerably higher (70%).

In Fig.2 (a)-(d), the experimental emission patterns measured following the 600°C annealing step give direct evidence of the degradation of the channeling effects. More precisely, while the overall anisotropy of all channeling patterns decreased considerably, also the relative intensities of the planar and axial effects changed, pointing towards changes in the Ag lattice sites. In fact, the best fits for these patterns [Fig.2 (e)-(h)] were obtained for approximately 46% of the Ag atoms at S_{Zn} sites with higher rms displacements of the order of 0.38–0.52 Å.

The behavior of the average fraction of Ag atoms at S_{Zn} sites and of the room temperature rms displacements as a function of the annealing temperature are presented in Figs.3 (a) and (b),

respectively. The results reveal that up to the 600°C vacuum annealing the fraction of Ag atoms at S_{Zn} sites increased somewhat to 46%, but the rms displacement increased considerably, changing from around 0.23–0.32 Å (400°C annealing) to 0.38–0.52 Å. These unusually large rms displacements, which also vary considerably perpendicular to the four investigated axes, could be a consequence of displacements along particular crystal directions. We therefore also explored the possibility in more detail that the Ag atoms are displaced towards the bond center (BC) or anti-bonding (AB) positions within the c -axis or towards the three BC or AB positions that are off the c -axis. We found that a fixed displacement of 0.3–0.5 Å from S_{Zn} to the off- c axis BC positions yielded a quality of fit that came close to but still was somewhat worse than the χ^2 due to the isotropic Gaussian rms displacements given above.

The last annealing step at 800°C, as was clearly evident from the loss of activity from the ZnO crystal, induced out-diffusion of around 30% of the Ag atoms. Despite this, apparently the fraction at S_{Zn} sites of the remaining Ag atoms did not change and also the rms displacements remained at high values. However, it is important to point out that the diffusion process may also have affected the derived Ag fractions at S_{Zn} sites, since the theoretical patterns used in the fitting procedure were generated considering the as-implanted depth profile. In order to evaluate possible effects on the Ag fractions and rms displacements, simulation results for a homogeneous depth profile from 0 to 5000 Å were also considered in the analysis. They revealed that, although hypothetical values of 200% were found for the Ag fractions at S_{Zn} sites, the rms displacements and their behavior with increasing annealing temperature remained similar to the results derived using as-implanted profiles. However, since the Ag depth profile is most likely no longer well defined after the highest annealing

temperatures, the values for those fractions are subject to greater uncertainty and we have marked them as less accurate in Fig. 3.

In order to explain the observed Ag behavior, several scenarios seem possible. One of them is, for instance, that Ag is only stable up to around 400°C on ideal substitutional sites, that it starts to diffuse at higher temperatures but is then trapped again by different crystal defects, leading to its incorporation on S_{Zn} sites with large rms displacements. Another possibility is that the large rms displacements occur on account of other defects that have been trapped by substitutional Ag, such as additional vacancies or interstitials.

4. Conclusions

Following the ^{111}Ag low dose room temperature implantation of a ZnO single-crystal, around 30% of the Ag atoms are substitutional at Zn sites with low root mean square displacements. This fraction did not significantly change during the annealing procedure up to 400°C, and no evidence was found for Ag at other regular, in particular well-defined interstitial, sites. A considerable increase of the Ag rms displacements from the S_{Zn} site was observed after the 600°C vacuum annealing. Finally, annealing at 800°C was accompanied by pronounced outdiffusion of Ag. The channeling patterns due to the ^{111}Ag atoms remaining in the sample still resulted from the occupancy of near-substitutional Zn sites with large rms displacements, but the fraction of Ag on these sites is subject to greater uncertainty.

5. Acknowledgements

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Figure Captions

Fig.1 – Angular distributions of the β^- particles emitted from ^{111}Ag in ZnO around the [0001] (a), $[\bar{1}102]$ (b), $[\bar{1}101]$ (c) and $[\bar{2}113]$ (d) directions following room temperature implantation. The best fits of the channeling patterns for each direction are also shown and correspond to approximately 30% of Ag atoms at S_{Zn} sites with rms displacements of 0.18 Å (e), 0.17 Å (f), 0.20 Å (g) and 0.26 Å (h).

Fig.2 – Emission channeling patterns around the [0001] (a), $[\bar{1}102]$ (b), $[\bar{1}101]$ (c) and $[\bar{2}113]$ (d) directions following the 600°C vacuum annealing step. The best fits for each direction are shown on (e)-(h).

Fig.3 – Fraction of Ag atoms at S_{Zn} sites (a) and their rms displacements perpendicular to the [0001], $[\bar{1}102]$, $[\bar{1}101]$ and $[\bar{2}113]$ directions (b) following 10 min annealing steps (in vacuum up to 800°C). The dashed and dotted lines represent the room temperature Zn and O vibration amplitudes, respectively.

Figure 1

Figure 2

Figure 3