PAC studies of implanted ^{111}Ag in single-crystalline ZnO

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The local environment of implanted ^{111}Ag ($t_{1/2} = 7.45\text{d}$) in single-crystalline [0001] ZnO was evaluated by means of the perturbed angular correlation (PAC) technique. Following the 60 keV low dose ($1 \times 10^{13} \text{ cm}^{-2}$) ^{111}Ag implantation, the PAC measurements were performed for the as-implanted state and following 30 min in vacuum annealing steps, at temperatures ranging from 200°C to 1050°C. The results revealed that 42% of the probes are located at defect-free S_{Zn} sites ($\nu_Q \sim 32 \text{ MHz}$, $\eta = 0$) in the as-implanted state and that this fraction did not significantly change with annealing. Moreover, a progressive lattice recovery in the near vicinity of the probes was observed. Different EFGs assigned to point defects were furthermore measured and a general modification of their parameters occurred after 600°C. The 900°C annealing induced the loss of 30% of the ^{111}Ag atoms, 7% of which were located in heavily damaged regions.

Keywords: ZnO, Ag, PAC, defects

1. Introduction

The problematic involved with the p-type doping of ZnO is one of the most active trends of investigation in this intrinsically n-type II-VI wurtzite semiconductor. The difficult or non-incorporation of acceptors on appropriate lattice sites and their association with defects are two of the main reasons for the low density of holes achieved in this material [1]. As a *Ib* element, Ag is one of the potential acceptors in ZnO if incorporated on substitutional defect-free Zn (S_{Zn}) sites. In previous studies, the incorporation of Ag at both S_{Zn} and interstitial sites (amphoteric dopant) was suggested [2]. Nevertheless, recent emission channelling investigations for the lattice site location of ^{111}Ag implanted into ZnO single crystals, revealed only one regular site for this element: the S_{Zn} site. In spite that, only 30% of the Ag atoms were found at S_{Zn} , there was no further evidence for Ag in the interstitial form. Moreover, the trapping of Ag by defects was suggested by the elevated root mean square displacements from the S_{Zn} site [3], motivating the investigation of ^{111}Ag near neighbourhood.

In this work, the annealing of point defects, in the local environment of implanted ^{111}Ag ($t_{1/2} = 7.45\text{d}$) into ZnO single crystals was evaluated by means of the Perturbed γ - γ Angular Correlation (PAC) technique. With this method, the Electric Field Gradient (EFG) at the ^{111}Ag site can be measured [4], providing information about the immediate lattice vicinity of the probe. Hence, structural disturbances, such as, dislocations and specific defects located in the ^{111}Ag atoms neighbourhood can be monitored.

2. Experimental details

A commercially available [0001] ZnO single crystal (CrysTec, hydrothermal growth) was homogeneously implanted with 60 keV ^{111}Ag atoms, up to a dose of $1 \times 10^{13} \text{ cm}^{-2}$, at the CERN/ISOLDE facility [5]. These implantation parameters correspond to a

projected range, straggling and peak concentration of 195 Å, 74 Å and 5×10^{18} at/cm³, respectively.

The time dependent perturbation of the angular correlation of the 97-245 keV cascade from ¹¹¹Cd, populated by the ¹¹¹Ag β-decay, was measured with a 4-BaF₂-detector setup. This perturbation results from the interaction between the quadrupole moment (Q) of the cascade's intermediate state ($t_{1/2} = 85$ ns, $I=5/2^+$) and the EFG at the probe site. Experimentally, for each EFG, the perturbation results in three observable frequencies that will be present in the experimental PAC perturbation function R(t) [4]. By fitting R(t), the coupling constant $v_Q = 2I(2I-1)\omega_Q/(6\pi) = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ can be determined and, thus, provide information about the EFG. In this formalism, the EFG is represented by a tensor, V_{ij} , where $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ are the principal components [4].

For the undisturbed crystalline wurtzite structure of [0001] ZnO, a unique EFG is expected with $\eta=0$ and oriented along the [0001] axis. The PAC measurements were therefore performed in the Raghavan geometry, with the [0001] direction positioned at $\theta = 45^\circ$ and $\phi = 90^\circ$, relatively to all detectors. In this way, not only v_Q and η can be extracted for each EFG, but also the orientation relatively to the crystal coordinates. Besides the characteristic lattice EFG, sensed by ¹¹¹Ag atoms located at undisturbed lattice sites, other EFGs induced by defects are likely to be found. The crystal was measured at room temperature in the as-implanted state and following the 200°C, 400°C, 600°C, 800°C, 900°C and 1050°C 30 min vacuum annealing steps.

3. Experimental results and discussion

In Figure 1a) - f), the R(t) and FFT functions obtained for the as-implanted state and following the 600°C and 900°C vacuum annealings, are presented. For all the annealing temperatures, approximately 55% of the probes were assigned to four different EFGs in the fitting procedure. The remaining 45% of the ¹¹¹Ag atoms are considered to be located in heavily damaged regions with undefined defects configuration, experiencing, thus, an EFG distribution. Figure 2a) and b) represent the annealing temperature dependence of v_Q , η , the fractions of ¹¹¹Ag (f_i) and attenuation (δ_i), for each EFG. In the as-implanted state $f_1 = 42\%$ of the ¹¹¹Ag atoms were found at defect-free S_{Zn} sites, experiencing the lattice symmetry EFG₁, which is characterized by $v_Q(1) \sim 32$ MHz, $\eta(1)=0$ and orientated along the [0001] axis ($\theta=45^\circ$ and $\phi=90^\circ$). In spite that at this stage $v_Q(1)$ was still attenuated by $\delta_1 \sim 11\%$, with increasing annealing temperature the lowest value of 0.02% was reached (Figure 2 b)). This happened already after the 800°C annealing, suggesting a local lattice recovery. Additionally, not only f_1 did not change considerably with the annealings, but also the results are in close agreement to the ¹¹¹Ag Emission Channelling experiments above referred, where $\sim 30\%$ of Ag was found at S_{Zn} sites [3].

Figure 1. $R(t)$ functions and FFT for the (a, b) as-implanted state and following the (c, d) 600°C and (e, f) 900°C vacuum annealings.

Figure 2. Temperature dependence of a) ν_Q and η and b) of the ^{111}Ag fractions f and δ . Above 900°C, the quoted fractions were equally normalized to account for 23% out-diffusion of ^{111}Ag , except for f_5 , as from this fraction only 7% out-diffused.

The results indicated that three more EFGs with high η , assigned to defects, were present in fractions ranging from 3% to 13%. These values proved to be quite stable throughout the annealing procedure, but no EFG orientation could be defined. While their asymmetry η was always elevated, the attenuations δ had a general tendency to decrease (Figure 2 a) and b)). EFG₂ revealed interesting parameters following the 200°C and 400°C annealings. In fact, with $\nu_Q(2) \sim 32$ MHz, close to the $\nu_Q(1)$ value, and large asymmetry $\eta(2) \sim 0.53$ - 0.61 , the presence of ^{111}Ag at S_{Zn} sites *seeing* a specific defect is

suggested. EFG₃ and EFG₄ are characterized by $\nu_Q(3) \sim 117$ MHz and $\nu_Q(4) \sim 162$ MHz up to the 400°C annealing. However, after the 600°C annealing a new configuration of the three defects is proposed by the modification of the corresponding parameters to $\nu_Q(2) \sim 52$ MHz, $\nu_Q(3) \sim 134$ MHz and $\nu_Q(4) \sim 182$ MHz, respectively. Moreover, the non-presence of EFG₂ after the 1050°C annealing and the f_1 increase, suggest that the ¹¹¹Ag atoms formerly associated to EFG₂ were incorporated in defect-free S_{Zn} sites.

It is also important to point out that the 900°C vacuum annealing induced the out-diffusion of approximately 30% of the ¹¹¹Ag atoms. One would be tempted to conclude that the lost ¹¹¹Ag atoms were the ones in undefined defect configurations (f_5), since they might more easily escape from the crystal. This hypothesis can be pondered by comparing the observable anisotropy for the 800°C and 900°C $R(t)$ functions, as if an increase of this value is observed, the above-referred assumption can be confirmed. Indeed, such an increase took place, but only by 7%. This indicates that from the 30% ¹¹¹Ag atoms that out-diffused, only 7% belonged to fraction f_5 (undefined defects configuration) and that, therefore, the remaining 23% came from the other ¹¹¹Ag fractions (defect-free S_{Zn} sites + 3 defect configurations). From our results and fitting procedure, it was not possible to assign these 23% to a specific fraction, for which, in Figure 2 b) the quoted fractions f_1, f_2, f_3 and f_4 above 900°C were equally normalized to account for this loss. Another curious aspect lays in the higher temperature annealing, at 1050°C, as it did not induce a further ¹¹¹Ag out-diffusion. The fact that this is observed only after the 900°C annealing is a suspicious indicator for only those atoms in a precise defect configuration, with a specific activation energy, would have escaped. Still, from our fitting results, we cannot draw such a conclusion, at least not for 23% of the lost atoms. In the future, EFG simulations will be undertaken, as well as PAC measurements of ¹¹¹Ag in metallic Ag, in order to define the origin of some of the defects observed in this study.

In resume, we have shown that in the as-implanted state 42% of the implanted ¹¹¹Ag atoms occupy defect-free S_{Zn} sites in single crystalline ZnO, experiencing the lattice symmetry EFG ($\nu_Q \sim 32$ MHz, $\eta = 0$), oriented along the [0001] axis. Annealing up to 1050°C in vacuum did not induce a significant variation of this fraction, but a progressive lattice recovery was observed in the near vicinity of the probes. Three other EFGs related with defects were measured, with fractions around 3%-13% and whose configuration changed following the 600°C annealing. The remaining 45% of the probes are considered to be experiencing a EFGs distribution, on a heavily damaged region. The 900°C vacuum annealing induced the out-diffusion of 30% of the ¹¹¹Ag atoms, 7% of which were the ones located in the damaged region. From our fitting results it was not possible to disentangle the origin of the remaining 23% lost. Furthermore, the higher temperature annealing did not result in Ag out-diffusion.

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