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

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The local environment of implanted ^{111}Ag ($t_{1/2}$ = 7.45d) in single-crystalline [0001] ZnO was evaluated by means of the perturbed angular correlation (PAC) technique. Following the 60 keV low dose (1×10^{13} 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 200ºC to 1050ºC. The results revealed that 42% of the probes are located at defect-free S_{Zn} sites (ν_Q~32 MHz, η=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 600ºC. The 900ºC 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 ($t_{1/2}$ = 7.45d) 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 1×10^{13} 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/cm^3, respectively.

The time dependent perturbation of the angular correlation of the 97-245 keV cascade from ^{111}Cd, populated by the ^{111}Ag β^--decay, was measured with a 4-BaF_2-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 $\nu_Q = 2I(2I-1)w_0/(6\pi) = eQV_{zz}/h$ 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 $\varphi = 90^\circ$, relatively to all detectors. In this way, not only ν_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 ^{111}Ag 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 200ºC, 400ºC, 600ºC, 800ºC, 900ºC and 1050ºC 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 600ºC and 900ºC vacuum annealings, are presented. For all the annealing temperatures, approximately 55% of the probes where assigned to four different EFGs in the fitting procedure. The remaining 45% of the ^{111}Ag 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 ν_Q, η, the fractions of ^{111}Ag (f) and attenuation (δ), for each EFG. In the as-implanted state f_1 = 42% of the ^{111}Ag atoms were found at defect-free S_{Zn} sites, experiencing the lattice symmetry EFG_1, which is characterized by $\nu_Q(1)$~32 MHz, $\eta(1)=0$ and orientated along the [0001] axis ($\theta=45^\circ$ and $\varphi=90^\circ$). In spite that at this stage $\nu_Q(1)$ was still attenuated by δ_1 ~11 %, with increasing annealing temperature the lowest value of 0.02% was reached (Figure 2 b)). This happened already after the 800ºC 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 ^{111}Ag Emission Channelling experiments above referred, where ~30% of Ag was found at S_{Zn} sites [3].

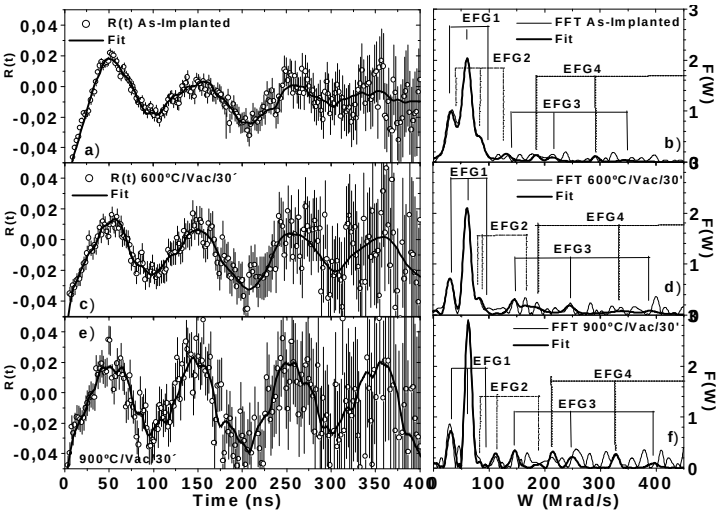

Figure 1. R(t) functions and FFT for the (a), b)) as-implanted state and following the (c), d)) 600°C and (e), f)) 900°C vacuum annealings.

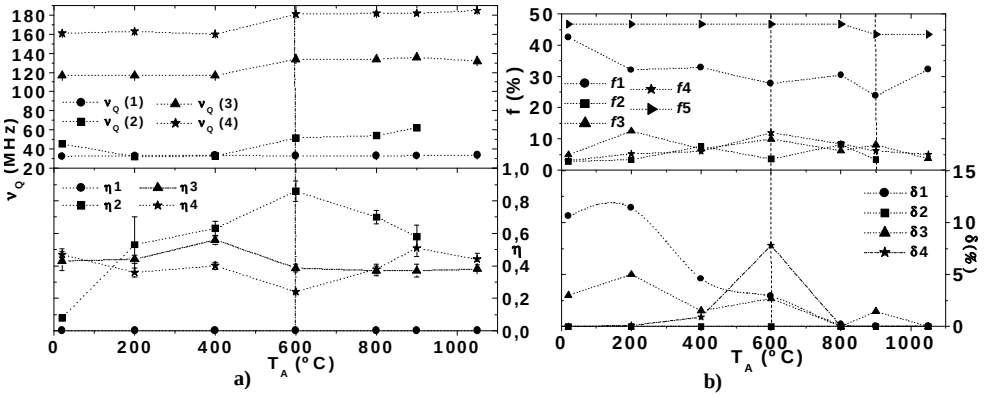

Figure 2. Temperature dependence of a) ν_Q and η and b) of the ^{111}Ag fractions f and δ. Above 900°C, the quoted fractions were equally normalized to account for 23% out-diffusion of ^{111}Ag, except for f_5, as from this fraction only 7% out-diffused.

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)). EFG_2 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. EFG_3 and EFG_4 are characterized by $\nu_Q(3) \sim 117$ MHz and $\nu_Q(4) \sim 162$ MHz up to the 400ºC annealing. However, after the 600ºC 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 EFG_2 after the 1050ºC annealing and the f_1 increase, suggest that the ^{111}Ag atoms formerly associated to EFG_2 where incorporated in defect-free S_{Zn} sites.

It is also important to point out that the 900ºC vacuum annealing induced the out-diffusion of approximately 30% of the ^{111}Ag atoms. One would be tempted to conclude that the lost ^{111}Ag 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 800ºC and 900ºC 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% ^{111}Ag atoms that out-diffused, only 7% belonged to fraction f_5 (undefined defects configuration) and that, therefore, the remaining 23% came from the other ^{111}Ag 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 900ºC were equally normalized to account for this loss. Another curious aspect lays in the higher temperature annealing, at 1050ºC, as it did not induce a further ^{111}Ag out-diffusion. The fact that this is observed only after the 900ºC 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 ^{111}Ag 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 ^{111}Ag 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 1050ºC 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 where measured, with fractions around 3%-13% and whose configuration changed following the 600ºC annealing. The remaining 45% of the probes are considered to be experiencing a EFGs distribution, on a heavily damaged region. The 900ºC vacuum annealing induced the out-diffusion of 30% of the ^{111}Ag 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.

[1] S.B.Zhang, J. Phys.: Condens. Matter 14 (2002) R881-R903

[2] J. Fan and R. Freer, Journal of Applied Physics 77 (9) (1995) 4795

[3] E.Rita *et al*, Physica B 340-342 (2003) 240-244

[4] H. Fraunfelder and R.M. Steffen, in: *α-, β-, γ–Ray Spectroscopy*, ed. K. Siegbahn, North-Holland, Amesterdam, 1965 p.997

[5] E. Kugler, D. Fiander, B. Jonson, H. Haas, A. Przewloka, H.L. Ravn, D.J. Simon, K. Zimmer, and the ISOLDE collaboration, Nucl. Instrum. Meth. Phys. Res. B 70 (1992) 41