Nanostructures and thin films of transparent conductive oxides studied by perturbed angular correlations


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1 IFIMUP and IN-Institute of Nanoscience and Nanotechnology, Departamento de Física e Astronomia da Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
2 Departamento de Física and CICECO, Universidade de Aveiro, Campus Universitário de Santiago, P-3810-193 Aveiro, Portugal
3 IST/ITN, Instituto Superior Técnico, Universidade Técnica de Lisboa, Estrada Nacional 10, 2686-953, Sacavém, Portugal
4 Centro de Física Nuclear da Universidade de Lisboa, Avenida Professor Gama Pinto 2, 1649-003 Lisboa, Portugal
5 Helmholtz-Institut für Strahlen- und Kernphysik, Universität Bonn, 53115 Bonn, Germany
6 Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany
7 Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense, E-28040 Madrid, Spain
8 Technische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany

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* Corresponding author: e-mail marcelo.barbosa@fc.up.pt, Phone: (+351) 22 04 02 362, Fax: (+351) 22 04 02 406

The versatility of perturbed angular correlations (PAC) in the study of nanostructures and thin films is demonstrated, namely for the specific cases of ZnO/CdZnO thin films and Ga2O3 powder pellets and nanowires, examples of transparent conductive oxides. PAC measurements as a function of annealing temperature were performed after implantation of 111mCd/111Cd (T1/2 = 48 min) and later compared to density functional theory simulations.

For ZnO, the substitution of Cd probes at Zn sites was observed, as well as the formation of a probe-defect complex. The ternary Cd0.16Zn0.84O revealed good macroscopic crystal quality but showed some clustering of local defects around the probe Cd atoms, which could not be annealed. In the Ga2O3 samples, the substitution of the Cd probes in the octahedral Ga-site was observed, demonstrating the potential of ion-implantation for the doping of nanowires.

1 Introduction In the past decades, the development of integrated circuits has been responsible for a true revolution in electronics and photonics applications. However, with increasing miniaturization following Moore’s law and the integration of nanotechnology in device applications, new and unpredicted properties are revealed, with potential applications to industry. Moreover, the modelling of these properties faces the fact that the smaller the devices get, the more they depend on the scale factor, geometry, symmetry and localized interactions of defects and impurities that can no longer be considered diluted and treated like “perturbations”. Therefore, in this highly integrated new world the small scale rules both new properties and new problems. The future of potentially relevant nano-materials relies on both tunable properties and on large-scale integration feasibility [1]. Nanostructures and thin film technologies might merge together where ion implantation is still envisaged as an integrated part of the processes. Still, ion implantation carries along with the benefits - universal dopant and profile
tuning - intrinsic nuisances, i.e., defect generation. Willing to contribute to the better understanding of doping and processing by ion beams, we present here two examples of studies performed with the nanoscopic Perturbed Angular Correlation technique (PAC). PAC probes the charge density distribution in the surroundings of chosen radioactive nuclei, thus allowing characterizing the probe’s real environment at the atomic scale. We have chosen to study ZnO and Cd$_x$Zn$_{1-x}$O thin films - aimed to cover luminescence wavelengths from UV to yellow [2] - and the technologically relevant high -K factor Ga$_2$O$_3$ nanostructures and Ga$_2$O$_3$ pellets [3]. Both materials belong to the family of transparent conductive oxides and the used PAC probe, $^{111}$Cd/$^{111}$Cd, is well suited to study the microscopic physical properties of these materials being an isoelectronic impurity in the case of ZnO and a possible p-type dopant in the case of Ga$_2$O$_3$.

For each case, we show how and to which extent the local environment of the implanted Cd is reconstructed to the one of the host crystalline matrix as a function of annealing temperature. We further attempt to identify local defects and the probes lattice site by comparing the experimental results with first principle simulations.

1.1 About the PAC technique

PAC has been widely used in solid state physics to study the local atomic environment of radioactive probe atoms since it accurately measures the electric field gradient ($EFG$) at a probe’s site, which is highly sensitive to the charge density distribution surrounding the nuclei [4]. In this method, a radioactive probe is introduced into the sample and the time dependence of the angular correlation between two emitted photons in a $\gamma-\gamma$ cascade decay is measured, with the first $\gamma$ starting the measurement and the second $\gamma$ stopping it. The hyperfine interaction of the $EFG$ at the probe site with the electric quadrupole moment $Q$ of the intermediate state of the cascade causes a time dependent perturbation in the emission direction of the second $\gamma$ with respect to the emission direction of the first $\gamma$. The time dependent oscillations in the anisotropic emission of the second $\gamma$ define the observable frequency $\omega_0$ which is proportional to the quadrupole interaction frequency $\omega_Q$.

$$\omega_0 = k \omega_Q, \quad \omega_Q = \frac{e Q V_{zz}}{4 I (2I-1) \hbar} \tag{1}$$

where $I$ is the spin and $Q$ is the electric quadrupole moment of the intermediate state, $V_{zz}$ is the principal component of the $EFG$ and $k$ is equal to 3(6) for integer(half-integer) spin. Since the $EFG$ is a traceless matrix, it can be completely described by the $V_{zz}$ component and the axial asymmetry parameter $\eta$ defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$ [4]. The existence of lattice imperfections or impurities causes different $EFG$s in the probe’s environment and thus a distribution of frequencies around a central value that induces an attenuation of the angular correlation. The distribution function, usually approximated by a Lorentzian, is then defined by the central frequency $\omega_0$ and the full width at half maximum $FWHM$.

1.2 Case studies: ZnO/Cd$_x$Zn$_{1-x}$O & Ga$_2$O$_3$

Zinc Oxide is subject of intense research due to its remarkable properties for optoelectronics, mainly for devices in the blue and UV range [5]. Its wide band-gap ($3.37 \text{eV}$ at room temperature) makes it desirable to adjust its electrical, optical and magnetic properties through doping with selective elements [6]. Furthermore, the possibility of growing pseudobinary compounds with MgO and CdO allows bandgap tuning and heterostructure growth. In particular, ternary Cd$_x$Zn$_{1-x}$O alloys allow band-gap engineering in a wide range that covers the UV-yellow spectral region [2]. However, ZnO and CdO have different crystalline structures, wurtzite and rock salt, respectively, being difficult to stabilize a wurtzite phase of Cd$_x$Zn$_{1-x}$O, which frequently results in phase separation [7,8]. The solubility of CdO in ZnO, besides being low, depends strongly on the growth conditions and technique that is used. Concerning PAC studies, ZnO bulk crystals have been studied using different probes [9] but, for technological purposes, thin films must be used. Thus, in this study, thin films of ZnO and Cd$_x$Zn$_{1-x}$O ($x = 0.16$) were investigated. Gallium oxide (Ga$_2$O$_3$) has the biggest band-gap among the transparent conductive oxides, 4.8 eV, making it interesting for photonics working in the UV and visible wavelength region[3,10–13]. However, in the case of ZnO, it is an intrinsic n-type semiconductor and it has been proven very difficult to obtain p-type doping, which is fundamental for technological applications. Nonetheless, its nanowires could be used as effective waveguides and optical doping using rare earth ions in-situ or by ion implantation has been demonstrated [3,13]. In this work we study the viability of ion implantation to incorporate dopants into these nanowires.

2 Technical details

The ZnO thin film (500 nm thick) was grown by molecular beam epitaxy (MBE) on an a-plane sapphire substrate at $T_s = 380^\circ\text{C}$ and subsequently annealed at $T_A = 650^\circ\text{C}$ for 5 minutes. The Cd$_{0.16}$Zn$_{0.84}$O thin film (200 nm thick) was grown at $T_s = 130^\circ\text{C}$ and annealed at $T_A = 400^\circ\text{C}$ for 4 hours. The film was grown on a 500 nm thick MgZnO buffer layer at $T_s = 380^\circ\text{C}$ on a-plane sapphire, the former serves to reduce the lattice mismatch and prevent the propagation of defects from the sapphire to the Cd$_{0.16}$Zn$_{0.84}$O layer [2]. The structural characterization of these samples has been reported previously [14]. Two different samples of $\beta$-Ga$_2$O$_3$ were used, a powder pellet and nanowires (both polycrystalline-like, consisting of a distribution of randomly oriented micro-crystals, from the point of view of the PAC measurement). The nanowires were grown from metallic gallium in a tube furnace using a vapour-solid growth mechanism reported elsewhere [3]. The grain size of the pellet was in the range of several microns whereas the nanowires’ length and thickness was up to tens of
Implantations were performed at ISOLDE/CERN with a 30 keV energy beam of radioactive $^{111m}$Cd/$^{111}$Cd ($T_{1/2} = 48\,\text{min}$) to low fluences of $\sim 5 \times 10^{11}\,\text{at./cm}^2$, at room temperature (RT). $\gamma$-$\gamma$ PAC experiments were done onto decay of $^{111m}$Cd ($\gamma_1 = 150\,\text{keV}$, $\gamma_2 = 245\,\text{keV}$) to $^{111}$Cd [15], whose intermediate state has an electric quadrupole moment of $Q = 0.83(13)\,\text{b}$ and spin $I = 5/2$ [16]. A BaF$_2$ 6-detector PAC setup was used [17], but when measuring single crystals only one 4-detector plane of this setup was selected, where the sample’s c-axis was oriented within the detector plane at $45^\circ$ with two 90° detectors ($M45$ setup). In the case of Cd$_{0.16}$Zn$_{0.84}$O, a complementary orientation was measured with the c-axis perpendicular to the 4-detector plane ($M90$ setup). The samples were annealed under air atmosphere during 10 minutes in a conventional tube furnace and the measurements were performed at $T_M = RT$.

X-ray diffraction (XRD) was used to determine the lattice parameters of the ZnO and Cd$_{0.16}$Zn$_{0.84}$O thin films yielding $a = 3.2405\,\text{Å}$ and $c = 5.2152\,\text{Å}$ for the ZnO and $a = 3.283\,\text{Å}$ and $c = 5.303\,\text{Å}$ for the Cd$_{0.16}$Zn$_{0.84}$O. The lattice parameters of the Ga$_2$O$_3$ powder samples and nanowires were previously found to be "relaxed" [18], i.e., with standard bulk parameters, thus the values $a = 12.23\,\text{Å}$, $b = 3.08\,\text{Å}$, $c = 5.80\,\text{Å}$ and $\beta = 107.3^\circ$, reported in ref.[10], were considered, which are in agreement with the optimum estimated atomic positions and lattice parameters found in the theoretical study of Ga$_2$O$_3$ done by F. Litimein et al. [19].

Additional characterization of the as-grown and as-implanted (and annealed) samples was carried out by Rutherford Backscattering Spectrometry (RBS/C) using a 2 MeV He$^+$ beam with 4 nA of current and a PIN diode detector at a backscattering angle of 165°.

To simulate the EFG at the probe’s site, a $3 \times 3 \times 2$ supercell of the wurtzite crystalline structure of ZnO was considered (72 atoms) with a $^{111}$Cd probe located at one of the equivalent Zn sites, using first the lattice parameters measured by XRD on the film and second the lattice parameters of bulk ZnO, $a = 3.2489\,\text{Å}$ and $c = 5.2053\,\text{Å}$, reported on ref.[20]. In the case of Ga$_2$O$_3$, a $1 \times 2 \times 2$ supercell of the $\beta$-Ga$_2$O$_3$ crystalline structure was considered (80 atoms), using the lattice parameters reported in ref.[10]. Since the Ga atoms have two non-equivalent sites, octahedral and tetrahedral, two simulations were performed, considering the $^{111}$Cd probe in each site. The simulations were performed via the L/APW+lo implementation of density functional theory (DFT), using the WIEN2k code [21]. The GGA-PBE exchange-correlation functionals and a cut-off value for the plane wave expansion of the wave function of $R_{\text{mt}}K_{\text{max}} = 7.0$ were considered, where $R_{\text{mt}}$ is the muffin-tin sphere radius and $K_{\text{max}}$ is the largest K-vector of the plane wave expansion of the wave function. For ZnO, 24 k-points in the irreducible Brillouin zone were used, and 15 in the case of Ga$_2$O$_3$. The convergence of the calculations was examined with respect to $R_{\text{mt}}K_{\text{max}}$ and to the number of k-points until the chosen values resulted in a convergence of the total energy of the crystal of less than 1 mRy. Relaxation of the atomic positions was done in a self-consistent way by minimizing the atomic forces to a maximum limit of 1 mRy/bohr. Smaller super-cells were attempted but the actual sizes were found to be the minimum required for achieving proper dilution of $^{111}$Cd at the DFT simulations.

3 Results and discussion

3.1 ZnO Figure 1 shows (left) the PAC experimental functions, the fits and (right) the corresponding cosine Fourier transform components from ZnO after implantation and as a function of the annealing temperature up to 900°C. The obtained fitting parameters are presented in Table 1. The data clearly shows the existence of a main position/situation for the probes revealed by one $EFG_1$ distribution that is characterized by the central frequency $\omega_0 = 26\,\text{Mrad/s}$ and $\eta = 0$. In the plot of the Fourier transform there are two dashed lines, corresponding to the observables $\omega_1 = 26\,\text{Mrad/s}$ and $\omega_2 = 52\,\text{Mrad/s}$, to mark the two main frequency components of $EFG_1$ for all measurements, as expected for a probe with spin 5/2 and $V_{zz}$ collinear with the sample’s c-axis. The existence of implantation defects is revealed by the important static distribution observed in the “as-implanted” sample that attenuates the frequency pattern at the $R(t)$ experimental function. In the absence of a second well-defined $EFG$ signature, we conclude that most of these implantation defects are not correlated with the probe nuclei but...
are randomly dispersed in the sample within the implantation and defect profiles. Upon increasing the annealing temperature to 800°C, in addition to the first fraction of probe nuclei with observable frequency \( \omega_{01} \), a second fraction starts to be observed indicating that defects are now present in more localized sites. On the one hand the width of the static distribution of the main fraction is reduced indicating a greater dilution of uncorrelated defects. On the other hand, some of the defects could come closer to the probes and eventually be trapped by the impurity Cd atom to originate \( EFG_2 \), for a certain fraction of probe atoms. The results are in good agreement with previous works in ZnO implanted with \( ^{111}\text{In} \) and measured at the same \( ^{111}\text{Cd} \) state [22–24], where M. E. Mercurio et al. [22] obtained a main fraction with \( \omega_{01} = 29.9(1) \text{Mrad/s} \) and a second fraction with \( \omega_{02} = 142(5) \text{Mrad/s} \) in ZnO powders, assigning the last to interstitial sites or vacancy-related sites. H. Wolf et al. [23] obtained a main fraction with \( \omega_{01} = 29.4(1) \text{Mrad/s} \) and a second fraction with \( \omega_{02} = 174(1) \text{Mrad/s} \) in ZnO single crystals, assigning the last to trapped oxygen-vacancies. P. Kessler [24] confirmed the assigning of the larger frequency \( EFG \) to next-neighbour oxygen vacancies, based on the fact that PAC measurements performed in different sites showed similar results, which can be justified by the existence of 4 (almost) equivalent positions for oxygen near the Zn atoms. In our case, due to the small fraction for \( EFG_2 \), we have not implemented a multi-\( EFG \) orientation fitting regarding this fraction. After annealing at 900°C the fraction of probes experiencing \( EFG_2 \) is decreasing suggesting that the probe-defect complex starts to dissociate at this temperature.

The smaller \( EFG_1 \) obtained for the thin film, compared to the one reported for bulk ZnO, can be explained by a bi-axial strain present in the epitaxial film. This assumption is confirmed by the DFT calculations, where the simulations carried out using the measured lattice parameters of the thin film resulted in a \( V_{zz} = 1.374 \times 10^{21} \text{V/m}^2 \) for the \( \text{Cd} \) probe in the \( \text{Zn} \) site, which is in perfect agreement with \( V_{zz} = 1.375(5) \times 10^{21} \text{V/m}^2 \) corresponding to the experimental frequency \( \omega_{01} \approx 26 \text{Mrad/s} \). Simulations using a variety of lattice parameters attributed for bulk ZnO were done in order to compare with the experimental results obtained by M. E. Mercurio et al. [22] \( (V_{zz} = 1.58(2) \times 10^{21} \text{V/m}^2 \) corresponding to the frequency \( \omega_0 = 29.9(1) \text{Mrad/s} \) and by H. Wolf et al. [23] \( (V_{zz} = 1.55(2) \times 10^{21} \text{V/m}^2 \) corresponding to the frequency \( \omega_0 = 29.4(1) \text{Mrad/s} \). However, the lattice parameters of the samples used in these works were not reported and quite an amount of different lattice parameters for bulk ZnO can be found [5, 9, 20]. Simulations were then performed with the parameters reported by H. Sowa and H. Ahsbahs [20], \( a = 3.2489 \text{Å} \) and \( c = 5.2053 \text{Å} \), resulting in a \( V_{zz} = 1.428 \times 10^{21} \text{V/m}^2 \). In the same article, a study of those parameters as a function of pressure was done, so using the parameters found for a pressure of 6.92 GPa, \( a = 3.2049 \text{Å} \) and \( c = 5.1216 \text{Å} \), resulted in a \( V_{zz} = 1.672 \times 10^{21} \text{V/m}^2 \). Hence, due to the fact that the \( V_{zz} \) is very sensitive to small variations of the lattice parameters and that \( V_{zz} \) increases, for \( \text{Cd} \) at the \( \text{Zn} \) site, with the decrease of the ratio \( c/a \), the measured \( V_{zz} \)‘s in ref.[22] and ref.[23] were probably done in samples with lattice parameters slightly different from the values used in the simulation.

The simulations confirm that the probes are incorporated on substitutional \( \text{Zn} \)-sites. Further DFT simulations considering different defect complexes are currently being performed in order to clarify the origin of \( EFG_2 \).

### Table 1

<table>
<thead>
<tr>
<th>Annealing</th>
<th>Fraction 1</th>
<th>Fraction 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \omega_0 )</td>
<td>( V_{zz} )</td>
</tr>
<tr>
<td>900°C</td>
<td>88%</td>
<td>26(1)</td>
</tr>
<tr>
<td>800°C</td>
<td>78%</td>
<td>26(2)</td>
</tr>
<tr>
<td>As implanted</td>
<td>100%</td>
<td>26(1)</td>
</tr>
<tr>
<td></td>
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**Figure 2** \(^{111}\text{Cd:Cd}_{16}\text{Zn}_{90.84}\text{O} \) \( \gamma-\gamma \) PAC from decay of \(^{111}\text{Cd} \). Study as a function of annealing temperature under air. \( T_M = RT \), Geometry: M45. (left) Counting rate ratio, \( R(t) \). (right) Frequencies extracted from \( R(t) \) after Fourier analysis.
Table 2 $^{111}$Cd: Cd$_{0.16}$Zn$_{0.84}$O fitting parameters, related to Fig. 2. $\omega_0$ and FWHM are given in $\text{Mrad/s}$ and $V_{zz}$ is given in $10^{12} \text{V/m}^2$.

<table>
<thead>
<tr>
<th>Annealing</th>
<th>$\omega_0$</th>
<th>$V_{zz}$</th>
<th>$\eta$</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>900$^\circ$C</td>
<td>37(1)</td>
<td>1.96(6)</td>
<td>0.5(1)</td>
<td>16.6(3)</td>
</tr>
<tr>
<td>800$^\circ$C</td>
<td></td>
<td></td>
<td></td>
<td>24.6(1)</td>
</tr>
<tr>
<td>600$^\circ$C</td>
<td></td>
<td></td>
<td></td>
<td>27.8(2)</td>
</tr>
<tr>
<td>400$^\circ$C</td>
<td></td>
<td></td>
<td></td>
<td>33.3(1)</td>
</tr>
<tr>
<td>As implanted</td>
<td></td>
<td></td>
<td></td>
<td>32.6(7)</td>
</tr>
</tbody>
</table>

crystal quality issues and the random distribution of Cd in the Cd$_{0.16}$Zn$_{0.84}$O lattice are present, even after annealing at 900$^\circ$C. We point out that in such kind of ternary compounds both Cd and Zn atomic distributions do not follow a regular super-cell-like pattern. The Cd concentration is big enough to clearly change the mean lattice parameters, but at the same time it will contribute to the non-unique EFGs that originate the large EFG distribution. The situation is clearly different from when implanting a small number of $^{111}$Cd atoms at the ppm concentration into the ZnO thin film. There, only implantation defects play a role and the Cd atoms themselves do not cause significant changes to the main ZnO EFG. Nevertheless, as can be seen by the fitting parameters in Table 2, the implantation defects contribution to the EFG distribution tend to be reduced as revealed by the decrease of the EFG distribution FWHM, with increasing annealing temperature. However, the attenuation of the curves remains high and little changes are observed in the PAC curves upon annealing.

The measurements indicate a higher central quadrupole frequency for the EFG distribution in Cd$_{0.16}$Zn$_{0.84}$O compared to ZnO, which has the same crystalline structure (wurtzite), and the existence of a non-zero axial asymmetry parameter. A different magnitude of the quadrupole interaction frequency could be expected since the lattice parameters expand with increasing Cd content in the ternary film but the latter does not explain the observed asymmetry of the EFG. Since it is difficult to determine frequencies and asymmetry parameters on such attenuated spectra, two different sample orientation experiments have been performed regarding the PAC setup detectors, previously referred as the M45 and M90 measurement geometries. If a main orientation of a central EFG persists within the EFG distribution, different amplitudes for each of the three harmonic components that characterise the EFG should be observed in a consistent way. Therefore, the obtained results and correspondent Fourier transforms for ZnO and Cd$_{0.16}$Zn$_{0.84}$O measured with the M45 setup and for Cd$_{0.16}$Zn$_{0.84}$O measured with the M90 setup, all of them after annealing at 900$^\circ$C, are shown in Figure 3. By only changing the orientation angles, both fits of the M45 and M90 measurements give consistent results concerning quadrupole frequency and asymmetry parameter in the Cd$_{0.16}$Zn$_{0.84}$O, thus confirming that the central quadrupole frequency is higher than that obtained for ZnO. Still the observed non-zero axial asymmetry parameter reveals that from the local point of view of the $^{111}$Cd atoms the observed EFG does not reflect the expected axial lattice symmetry. This is most likely due to the incorporation of the implanted Cd ions in lattice environments, which were strongly distorted by the implantation defects and/or imperfections in the original lattice structure. These distortions around the probes are thermally very stable and annealing up to 900$^\circ$C provides only minor changes in the PAC curves. In order to get additional information on the macroscopic crystal quality, before and after implantation and annealing, RBS/C measurements were performed.

Figure 3 $\gamma$-$\gamma$ PAC data of ZnO and Cd$_{0.16}$Zn$_{0.84}$O annealed at 900$^\circ$C; from decay of $^{111}$Cd. a) ZnO, M45 setup. b) Cd$_{0.16}$Zn$_{0.84}$O, M45 setup. c) Cd$_{0.16}$Zn$_{0.84}$O, M90 setup.
ing at 900°C [25]. In general, the RBS/C measurements show that the overall crystal symmetry and single crystalline character of Cd_{x}Zn_{1-x}O is preserved after implantation and annealing and no indications of phase separation due to the transformation of wurtzite to rocksalt phase are observed. PAC, on the other hand, reveals that very stable local distortions or defect complexes are formed in the implanted Cd probe’s neighborhood and that thermal annealing does not improve this situation. The Cd-loss evidenced by RBS at the highest annealing temperature does not seem to influence the PAC results measured at the remaining 111mCd/111Cd probe atoms, which further emphasizes the existence of highly stable defect complexes. Nonetheless, both RBS/C and PAC reveal the inefficiency of post-implant annealing treatments for Cd_{x}Zn_{1-x}O defect removal.

### 3.3 Ga_{2}O_{3}

The results for the pellet, Fig. 5a/Table 3, and for the nanowires, Fig. 5b/Table 4, are very similar, with two different fractions being observed, a EFG_{1} frequency distribution characterized by a central frequency $\omega_{01} \approx 115 \text{Mrad/s}$ (corresponding to $V_{zz} = 6.08(5) \times 10^{21} \text{V/m}^2$), $\eta_1 = 0$ and almost nil FWHM_{1}, and a EFG_{2} characterized by a bigger quadrupole frequency, $\omega_{02} \approx 140 \text{Mrad/s}$ ($V_{zz} = 7.40(5) \times 10^{21} \text{V/m}^2$), $\eta_2 = 0$, with a high static EFG distribution. In the Fourier transforms (right side of Figures 5a and 5b), $\omega_{01}$, 2$\omega_{01}$ and 3$\omega_{01}$ are represented for EFG_{1}.

By comparing the $V_{zz}$ obtained from DFT simulations (Table 5) to the experimental values, a perfect match is found for the first fraction (EFG_{1}) with the calculations assuming that the Cd probe is located in an octahedral Ga-site, where the experimental $V_{zz}$ is only $\sim 1\%$ different from the simulation. However, the second fraction does not correspond to the substitutional tetrahedral site. The total energy of the crystal simulated for the Cd probe in the octahedral Ga-site was 0.47 eV less than for the Cd probe in the tetrahedral Ga-site, hinting a preference of the probe for the octahedral site. Moreover, the distance to the nearest neighbours for the octahedral site is larger than for the tetrahedral site (Table 5), suggesting that the implanted 111mCd probes tend to occupy the Ga sites at the largest atomic position. The fact that, at the octahedral site, there are 6 oxygen first neighbours with distances between 2.115 Å and 2.218 Å, while at the tetrahedral site there are 4 oxygen neighbours with distances between 1.803 Å and 1.853 Å, allows an easier accommodation of the Cd ion in the first site. A further observation should be done to the fact that Ga^{3+} has an ionic radius of 0.62 Å while Cd^{2+} has an ionic radius of 0.95 Å, thus suggesting the preference of Cd incorporation in the octahedral site, where more space is available. As for the existence of the second fraction, revealing a highly attenuated EFG, it is probably due to remaining implantation defects, which could not be annealed. A previous study of Ga_{2}O_{3} implanted with 111In and also measured on 111Cd was performed by A. F. Pasquevich et al. [26]. They report three different EFGs, two being similar to those observed by us. It has to be noted that PAC using the 111In probe suffers from strong dynamic attenuation of the PAC spectra at RT due to so called “after effects” caused by the electron capture decay of the 111In probe [26]. Therefore, Pasquevich et al. only see well defined PAC patterns for measurements at high temperatures (> 500°C) where electron recombination is faster and after effects do not interfere. Like us, they attributed the $\omega_{01} \approx 113 \text{Mrad/s}$ frequency to octahedral sites but they interpret the frequencies $\omega_{01} \approx 113 \text{Mrad/s}$ and $\omega_{02} \approx 132 \text{Mrad/s}$ as two different charge states (ionized and neutral, respectively) of the Cd acceptor. Since our measurements show those frequencies at room temperature where a negligible number of deep Cd acceptors should be ionized we tend to assign EFG_{1} to the un-ionized Cd acceptor on the octahedral site and EFG_{2} to sites influenced by residual implantation defects. Additional studies using higher annealing temperatures as well as a systematic study at different measuring temperatures is needed for a final assignment of EFG_{2}. Finally, Pasquevich et al. report a third EFG - absent in our measurement - with $\omega_{01} \approx 182 \text{Mrad/s}$ which they assign to Cd on tetrahedral sites [26]. This assignment, however, is in disagreement with our simulation results predicting a smaller EFG for the tetrahedral site than for the octahedral site (see Table 5).

### 4 Conclusions and perspectives

The usefulness of PAC in the study of nanostructures and thin films was demonstrated, allowing the observation of the local atomic environment around the probe and thus giving information about the lattice structure and probe’s site. Two different case studies were analyzed, ZnO/Cd_{x}Zn_{1-x}O thin films and a Ga_{2}O_{3} powder pellet and Ga_{2}O_{3} nanowires, all measured after implantation of 111mCd/111Cd ($T_{1/2} = 48 \text{min.}$). In the ZnO...
Cd lattice geometry of the and confirmed the high sensitivity to small changes in the calculations performed with the measured lattice parameters and justifying this difference in the frequencies. DFT calculations with the measured lattice parameters showed excellent agreement with the experimental results in the studied films compared to the results found on the literature for bulk samples, but XRD measurements showed the existence of two different fractions, where the first one is attributed to the clustering of defects close to the probe, and on the ternary alloy where the \( \frac{EFG}{Zn} \) appeared after annealing and was attributed to the trapping of a defect, possibly an oxygen vacancy, in the vicinity of the probe. The ternary alloy \( \text{Cd}_{0.16}Zn_{0.84}O \), although having a wurtzite structure similar to ZnO, showed higher quadrupole frequencies, possibly due to the expansion of the lattice parameters with the \( \text{Cd} \) content, as well as a non-zero asymmetry parameter and large static distributions in the \( EFG \), which were attributed to the clustering of defects close to the probe, even after annealing. The nontrivial differences observed at the nanoscopic scale between high-quality epitaxial thin films of \( \text{ZnO} \), where \( \frac{EFG}{\text{ZnO}} \) appears as a highly diluted probe, and on \( \text{Cd}_{x}Zn_{1-x}O \) alloy where the \( \text{Cd} \) is at the % range, encourage a systematic study for different concentrations, from highly diluted to the % range, in fine films of \( \text{ZnO} \) at the nanoscopic scale between high-quality epitaxial thin films of \( \text{ZnO} \), where \( \frac{EFG}{\text{ZnO}} \) appears as a highly diluted probe, and on \( \text{Cd}_{x}Zn_{1-x}O \) alloy where the \( \text{Cd} \) is at the % range, encourage a systematic study for different concentrations, from highly diluted to the % range, in fine films of \( \text{ZnO} \). In the \( \text{Ga}_{2}O_{3} \) case, two different fractions were observed, as have been previously found for bulk samples. The smaller \( EFG \) was attributed to \( \text{Cd} \) probes on undisturbed substitutional sites. A smaller quadrupole interaction frequency was obtained in the studied films compared to the results found in the literature for bulk samples, but XRD measurements showed different lattice parameters (\( a = 3.2405 \text{ Å}, c = 5.2152 \text{ Å} \)) than the values for bulk samples (\( a = 3.2489 \text{ Å}, c = 5.2053 \text{ Å} \)) [20], revealing a different strain state in the thin film and justifying this difference in the frequencies. DFT calculations performed with the measured lattice parameters showed excellent agreement with the experimental results and confirmed the high sensitivity to small changes in the lattice geometry of the \( EFG \) probed by the radioactive \( \text{Cd} \) atoms incorporated at \( \text{Zn} \)-sites in the thin films. The larger \( EFG \) only appeared after annealing and was attributed to the trapping of a defect, possibly an oxygen vacancy, in the vicinity of the probe. The ternary alloy \( \text{Cd}_{0.16}Zn_{0.84}O \), although having a wurtzite structure similar to \( \text{ZnO} \), showed higher quadrupole frequencies, possibly due to the expansion of the lattice parameters with the \( \text{Cd} \) content, as well as a non-zero asymmetry parameter and large static distributions in the \( EFG \), which were attributed to the clustering of defects close to the probe, even after annealing. The nontrivial differences observed at the nanoscopic scale between high-quality epitaxial thin films of \( \text{ZnO} \), where \( \frac{EFG}{\text{ZnO}} \) appears as a highly diluted probe, and on \( \text{Cd}_{x}Zn_{1-x}O \) alloy where the \( \text{Cd} \) is at the % range, encourage a systematic study for different \( \text{Cd} \) concentrations, from highly diluted to the % range, in fine increasing steps, aiming the observation and identification of defects forming and segregating with increasing \( x \). In the \( \text{Ga}_{2}O_{3} \) case, both the powder pellet and the nanowires showed the existence of two different fractions, where the first one is attributed to \( \text{Cd} \) probes in the substitutional octahedral \( \text{Ga} \)-site and the second one is not understood, but probably results from the existence of residual implantation defects that could not be annealed. Nonetheless, the

<table>
<thead>
<tr>
<th>Atomic site</th>
<th>Distance nearest neighbours</th>
<th>( EFG ) (V/m²)</th>
</tr>
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<tbody>
<tr>
<td>Octahedral</td>
<td>2.115 - 2.218</td>
<td>6.02 × 10²¹</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>1.803 - 1.853</td>
<td>4.67 × 10²¹</td>
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</tbody>
</table>

**Figure 5** PAC curves and Fourier transforms for \( \text{Ga}_{2}O_{3} \) pellets (a) and nanowires (b) for as-implanted samples and after annealing at 800°C. \( T_M = RT \), Geometry: \( M\overline{4}5 \). For \( T_A = 800°C \) in (a), besides \( R(t) \), fraction 1 is represented in orange and fraction 2 in red.

**Table 3** \( ^{111}\text{Cd}\text{Ga}_{2}O_{3} \) powder pellet fitting parameters, related to Fig.5a. \( \omega_0 \) and \( FWHM \) are given in Mrad/s and \( V_{zz} \) is given in \( 10^{21} \text{ V/m}^2 \).

<table>
<thead>
<tr>
<th>Annealing</th>
<th>Fraction 1</th>
<th>Fraction 2</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>( \omega_0 )</td>
<td>( V_{zz} )</td>
</tr>
<tr>
<td>800°C</td>
<td>41%</td>
<td>115(2)</td>
</tr>
<tr>
<td>As implanted</td>
<td>10%</td>
<td></td>
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</table>

**Table 4** \( ^{111}\text{Cd}\text{Ga}_{2}O_{3} \) nanowires fitting parameters, related to Fig.5b. \( \omega_0 \) and \( FWHM \) are given in Mrad/s and \( V_{zz} \) is given in \( 10^{21} \text{ V/m}^2 \).

<table>
<thead>
<tr>
<th>Annealing</th>
<th>Fraction 1</th>
<th>Fraction 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \omega_0 )</td>
<td>( V_{zz} )</td>
</tr>
<tr>
<td>800°C</td>
<td>52%</td>
<td>115(1)</td>
</tr>
<tr>
<td>As implanted</td>
<td>9%</td>
<td></td>
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</table>
similarity between the results for the powder pellet and the nanowires demonstrates that efficient doping of nanowires by ion implantation is conceivable.

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References