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Cd doping of AlN via ion implantation studied with perturbed angular correlation

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AlN with a wide bandgap of 6.2 eV is a promising candidate for ultraviolet light-emitting diodes and laser diodes. However, the production of the required p-type AlN is still challenging. As a possible dopant Cd was suggested among other Group II atoms (Be, Mg, and Zn).

In this study the annealing condition of implanted Cd in AlN was investigated with the method of the perturbed angular correlation (PAC). Therefore radioactive ¹¹⁷Cd or ^{111m}Cd ions were implanted into thin AlN films on sapphire substrate with an energy of 30 keV and fluences in the range of 10¹¹ ions/cm².

After thorough annealing with a proximity cap of the same material most of the Cd-probes occupy substitutional lattice sites and almost all implantation damage can be annealed. This results in a distinct frequency in the PAC spectra which increases with temperature. In contrast to the formation of an indium nitrogen-vacancy complex observed with the probe ¹¹¹In on substitutional Al-sites no defects are bound to substitutional Cd impurities.

1 Introduction AlN with a wide bandgap of 6.2 eV is a possible candidate for deep UV-LEDs and laser diodes. The predicted minimal emission wavelength is in the range of 200 nm. In 2006 Taniyasu et al. [1] showed that the fabrication of AlN-LEDs is indeed possible, although the efficiency was very low. As in all Group III nitrides the p-doping proved to be difficult, which was achieved by substituting Al with Mg. Due to the deep acceptor level of Mg ($E_A = 0.5$ eV) such a high Mg content is required to obtain efficient LEDs that solubility problems occur. To overcome this problem other group II atoms were suggested: Be, Zn or Cd [2].

Cd is a well known perturbed angular correlation (PAC) probe [3]. With this method electric field gradients (EFG)

at the probe site are measured. The radioactive isotopes that are used as probes are implanted into the samples. This allows to study complex-formation of point defects and the probes as well as implantation defects. In this work we present temperature dependent PAC measurements of ^{111m}Cd and ¹¹⁷Cd implanted into AlN. The obtained results are compared to previous ¹¹¹In measurements, that showed a complex of ¹¹¹In and a nitrogen-vacancy that forms during the annealing of the samples and is stable up to high temperatures [4]. Furthermore, it can be shown, that this complex is not formed with Cd when measured at room temperature [5], which indicates that Cd traps no defects. In this work we investigate the incorporation of Cd in the

AlN lattice and the stability of the Cd site and its environment at different temperatures between 11 K and 873 K.

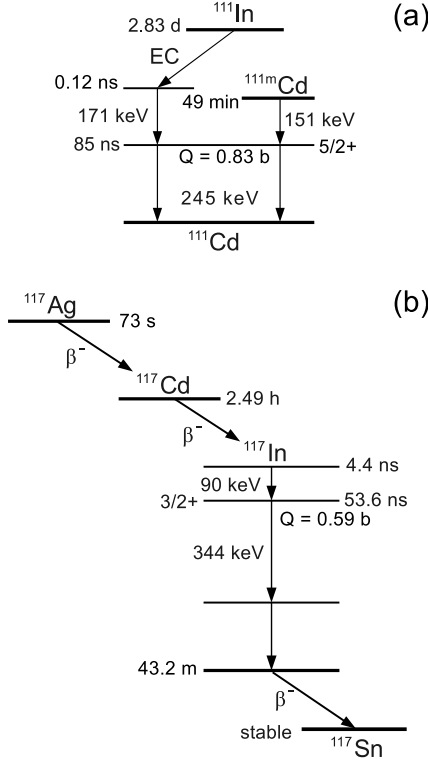


Figure 1 Simplified decay schemes [6,7] of the radioactive isotopes ^{111}In , $^{111\text{m}}\text{Cd}$ (a) and ^{117}Cd (b). The actual measurement is at Cd or In intermediate states, respectively. During annealing and the actual measurement the ^{117}Ag has already decayed to ^{117}Cd due to the short half-life of 73 s.

2 Methods The local environment of Cd in AlN was investigated with the time dependent PAC. With this method EFGs at radioactive probe sites are determined. The time dependent angular correlation between two γ s is measured at 90° and 180° . The first γ populates an intermediate state (PAC-state) and starts the measurement. The second γ of this state's decay is the stop signal. The simplified decay schemes of the used probes $^{111\text{m}}\text{Cd}$ and ^{117}Cd are shown in Fig. 1. The hyperfine interaction between the quadrupole moment Q of the intermediate state and an EFG causes a time dependent oscillation of the probability to measure the second γ . A detailed description of this method can be found in [3]. As a first step of the data treatment, the ratio $R(t)$ of the 180° and 90° spectra is computed (Eq. 1).

$$R(t) = 2 \frac{N_{180^\circ}(t) - N_{90^\circ}(t)}{N_{180^\circ}(t) + 2 \cdot N_{90^\circ}(t)} \quad (1)$$

$$R(t) \propto \sum_{n=0}^N s_n \cdot \cos(n\omega_0 t) \cdot e^{-\omega_0 \delta t} \quad (2)$$

$$N = 3 \text{ for } ^{111\text{m}}\text{Cd}, ^{111}\text{In} \text{ and } N = 1 \text{ for } ^{117}\text{Cd}$$

Then Eq. 2 is fitted to the ratio function $R(t)$. N depends on the spin of the PAC-state. For the $^{111\text{m}}\text{Cd}$ and ^{111}In PAC-state the spin is $5/2$ and $N = 3$, and for the ^{117}Cd PAC-state the spin is $3/2$ and $N = 1$. The s_n are weighting factors that depend on the spin of the PAC-state and the angle between start- γ and EFG. δ describes the distribution of the oscillation ω_0 . Now the spin independent quadrupole interaction frequency (QIF) ν_Q is defined as:

$$\nu_Q = \frac{eQV_{zz}}{h} \propto \omega_0 \quad (3)$$

ν_Q depends on the quadrupole moment Q of the intermediate state: $Q = 0.83(13)\text{ b}$ for ^{111}In and $^{111\text{m}}\text{Cd}$ [6] and $Q = (-)0.59(1)\text{ b}$ for ^{117}Cd [7]. From ν_Q the magnitude of V_{zz} the principal component of the EFG can be derived. Hence, the obtained oscillation ω_0 is proportional to the EFG at the probe site (Eq. 3). The damping δ can be attributed to the overall crystal quality, because small changes in the environment of the probes caused by distant defects influence the EFG. A perfect crystal has a δ of 0%. In reality damping of 1% can be observed for well annealed samples (e.g. ^{111}In in ZnO). Additional probe sites, for example point defects cause different and additional EFGs, and more frequencies are observed in the ratio function $R(t)$.

The $^{111\text{m}}\text{Cd}$ and ^{117}Ag ions (that decay to ^{117}Cd) were implanted with an energy of 30 keV and fluences ranging from 10^{11} to 10^{12} ions/cm² at the ISOLDE facility at CERN. Subsequently the 3 μm thick AlN films on sapphire substrate were annealed for 600 s at 1223 K. To avoid the out-diffusion of nitrogen, a proximity cap of the same material was used in addition to flowing nitrogen. The following PAC measurements were taken with two different spectrometers, a 6 BaF₂-detector setup [8] for the ^{117}Cd and a conventional 4 BaF₂-detector setup for the $^{111\text{m}}\text{Cd}$ measurements. Either a furnace with flowing nitrogen or a cryostat can be fitted between the detectors to cover temperatures between 873 K and 11 K.

3 Results and discussion

3.1 ^{117}Cd in AlN Selected ratio functions $R(t)$ of the ^{117}Cd measurements at different temperatures are shown in Fig. 2. The data (hollow dots) can be described with one fraction (the fit to the data is shown as a solid black line). In Fig. 4 the fitted parameters are shown. The obtained QIF of $\nu_Q = 40.8(5)\text{ MHz}$ at 11 K increases slightly with temperature to $\nu_Q = 42.0(5)\text{ MHz}$ at 873 K (Fig. 4 (a)). The damping δ increases from 5.3(7)% at 11 K to 9.8(7)% at room temperature and decreases again to 4.9(6)% at 873 K (Fig. 4 (b)). These results indicate, that the probes are in a unique environment. From RBS/ Channeling measurements it is known that Cd and the implanted Ag occupy Al-sites [9].

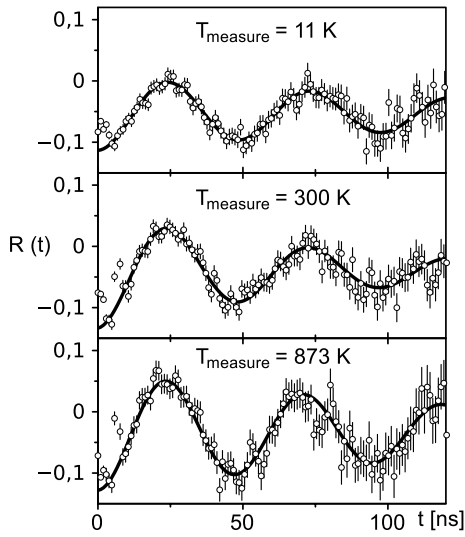


Figure 2 Ratio function $R(t)$ of ^{117}Cd implanted into AlN measured at selected temperatures. The observed QIF can be described with a single probe site.

The observed QIF at the Al-site therefore most likely results from the wurtzite structure of AlN. An EFG with the principle axis along the c-axis is caused by the asymmetry of the charge distribution by the lattice itself. Moreover, the low damping of the QIF [10] at the undisturbed probe site shows, that most of the implantation damage is annealed.

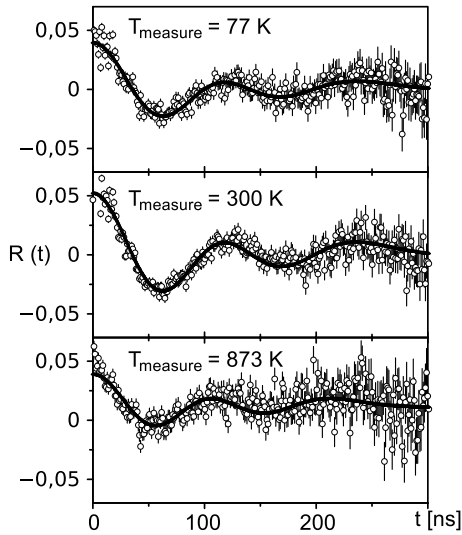


Figure 3 Ratio function $R(t)$ of $^{111\text{m}}\text{Cd}$ implanted into AlN measured at selected temperatures. The observed QIF can be described with a single probe environment.

3.2 $^{111\text{m}}\text{Cd}$ in AlN and comparison with ^{111}In in AlN The ratio functions of the temperature dependent $^{111\text{m}}\text{Cd}$ measurement are shown in Fig. 3. Again the data can be described with one fraction. In Fig. 4 (a) the temper-

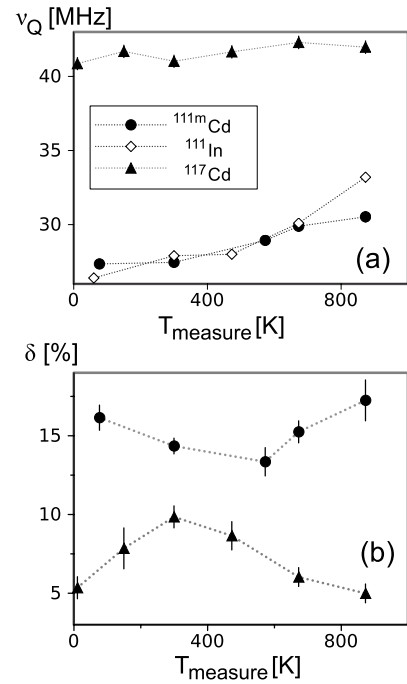


Figure 4 Temperature dependence of the QIF ν_Q (a) and the damping δ (b). The QIF of all probes increases with temperature. The QIF of ^{111}In and $^{111\text{m}}\text{Cd}$ are similar, which is expected for Cd on Al sites, since the measurement is done at the same PAC-state.

ature dependence of the QIF is shown; QIF increases with temperature from 27.3(3) MHz at 77 K to 30.5(4) MHz at 873 K. The damping decreases from 16.1(8)% at 77 K to 13.3(9)% at 473 K and increases again to 17(2)% at 873 K (Fig. 4 (b)).

The increase of the QIF with temperature is similar to that of the QIF of ^{111}In in AlN also given in Fig. 4, although a second probe environment with a much larger EFG is observed [4]. Due to the fact, that the PAC-state is the same in both probes, this is an additional evidence, that Cd is incorporated on substitutional Al-sites which is known for In. $^{111\text{m}}\text{Cd}$ is identified by the different start energy of 151 keV and the much shorter half life of the initial excited state of $^{111\text{m}}\text{Cd}$. In addition the production and ionisation at ISOLDE insures, that $^{111\text{m}}\text{Cd}$ is implanted into the samples and not ^{111}In . Therefore the measurement is not affected by a possible co-implantation with ^{111}In . Compared to the ^{117}Cd measurements the crystal quality after annealing is not as good. The reason could be different annealing conditions. Because of the short half-life of 49 min of $^{111\text{m}}\text{Cd}$ the sample treatment was difficult. In addition, RBS measurements indicate that the incorporation of Ag into substitutional sites during annealing (^{117}Ag was implanted that decays to ^{117}Cd) in AlN is better than that of Cd [9].

The increase of the QIF with temperature is observed in many compound semiconductors (AlN, GaN, ZnO) [4].

Wolf et al. [11] suggested to explain this with the formation of charged defects in ZnO due to the rising temperature. The resulting increase of charge carrier density amplifies the EFG. This was applied by Sato et al. [12] to determine the activation energy of the donor In in ZnO and could also be possible for AlN and other semiconductors. However, in this study we cannot comment on the exact nature of the observed change of the EFG, because ^{111m}Cd is measured at a Cd PAC-state and ^{117}Cd at In. From DFT calculations it is known [13] that small changes in the exact probe position have a large influence on the EFG. Since ^{117}In and ^{111}Cd differ in size and charge state it is not possible to deduce the exact reason for the EFG change.

4 Conclusion Thin films of AlN were implanted with the Cd PAC-probes $^{117}\text{Ag}(^{117}\text{Cd})$ and ^{111m}Cd . It can be shown, that most of the Cd is incorporated on substitutional Al sites and most of the implantation damage can be annealed. Furthermore, the Cd probes trap no point defects in contrast to implanted In in AlN. We conclude that Cd is incorporated on a regular undisturbed lattice site where it is stable over a broad temperature range and therefore a promising candidate for p-type AlN.

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