Proposal to the ISOLDE and Neutron Time-of-Flight Committee

The role of In in III-nitride ternary semiconductors

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ABSTRACT

This proposal aims to study the role of In in the outstanding efficiency of luminescent devices based on group III-nitride ternary semiconductors. To study the microscopic environments of In in GaInN and AlInN, Perturbed Angular Correlation (PAC) experiments will be performed using the PAC-probes ^{111m}Cd(^{111}Cd), ^{115}Cd(^{115}In) and ^{117}Cd(^{117}In). Temperature dependent PAC measurements using the ^{111}In(^{111}Cd) probe indicated that In in GaN and AlN forms a complex with a defect, possibly a nitrogen vacancy (V_N), which is stable up to high temperatures and might be involved in the luminescence mechanisms. Analysing these results two questions arose: 1. Does the fact that the actual measurement is performed with the daughter nucleus ^{111}Cd (being an acceptor) influence the probe-defect interaction? This question can be enlightened by performing measurements with the complementary probe ^{117}Cd(^{117}In). 2. What is the significance of *after effects* that can occur when the mother nucleus ^{111}In is decaying via electron capture leaving a hole in the electron shell of the probe? This effect can be excluded by measurements using the ^{111m}Cd(^{111}Cd) which decays via the same intermediate state. Additional e^--γ PAC experiments using conversion electrons, from the same decay of ^{111m}Cd, will provide additional and specific information on the influence of *after effects*.
Detailed temperature dependent PAC measurements with all three probes will be performed in GaN and AlN. Additionally, by varying the sample treatment (e.g. the post-implant annealing conditions or pre-implantations of stable In/Cd) the nature of the trapped defect will be studied.
Measurements using the ^{115}Cd(^{115}In) probe will furthermore allow the determination of the sign of the quadrupole interaction, an important parameter when comparing experimental results with density functional calculations of the electric field gradient.

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CERN-INTC-2008-038 / INTC-P-251
04/10/2008

1. Introduction

Due to their wide and direct band gaps, group-III nitrides are promising semiconductor materials for a wide range of technological applications in optoelectronics, as well as high power- high frequency- and high temperature electronic devices[1]. Of special interest is the ternary alloy InGaN which is used in active layers of LEDs and laser structures[2]. Despite the successful commercialization of these devices many basic questions on the mechanisms of light emission remain unanswered. A subject of intensive scientific discussion is the fact that the intense luminescence from InGaN based LEDs and laser diodes is relatively insensitive to the large density of defects, mainly threading dislocations[3]. A widely accepted explanation for this behaviour is the localization of excitons at regions with minima in the potential caused for example by compositional fluctuations. Indium rich nanoclusters[4], local bandgap variations due to compositional[5] or strain[6] inhomogeneities as well as microstructures[7] have also been proposed to be the origin of exciton localization at radiative traps preventing them from diffusing to nonradiative recombination centres[8]. Recently, it was shown by Extended X-ray Absorption Fine Structure (EXAFS) that *non-random* aggregation of In atoms occurs in InGaN epilayers[9]. The degree of phase segregation was shown to decrease with increasing InN concentration. Since this phenomenon is accompanied by a decrease of luminescence efficiency these regions of weak phase segregation were proposed to act as efficient localization centres for excitons.

Recently, the interest in another nitride ternary compound, AlInN, is rapidly raising due to the possibility of growing AlInN with an InN fraction of around 17% lattice-matched to GaN. At the same time AlInN has different optical, chemical and electrical properties opening new options for devices with strain-free nitride heterostructures[10,11]. Again, the In-containing alloys show superior optical properties to their AlGaN counterparts[8,10].

It is interesting to note that in all cases Indium plays an important role in one way or another. The Perturbed Angular Correlation (PAC) technique provides a powerful tool to examine the lattice environment of an In probe on a microscopic scale. Previous studies with the PAC-probe ^{111}In/^{111}Cd in GaN and AlN revealed an unexpected, reversible behaviour of its local structure with temperature[12,13,14]. After implantation and annealing GaN and AlN at 1000ºC only a fraction of the In probes was found in undisturbed substitutional cation sites while a large fraction is subjected to a strong electric field gradient typical for a point defect trapped at the probe atom. However, when the measurements were performed at higher temperature the undisturbed substitutional fraction increased until all probes are found in regular sites. Surprisingly, this behaviour is fully reversible when the temperature is decreased again (see Fig. 1).

The results suggest as a possible explanation that a large fraction of In impurities in GaN and AlN form a stable complex with a nearest neighbour nitrogen vacancy in the <0001> position. This model is supported by recent theoretical calculations which suggest that V_N is the most abundant defect in GaN for all positions of the Fermi level[15] and the defect complex might be the radiative exciton trapping centre long sought after to explain the high luminescence efficiency in nitrides and/or a seed for phase segregation through In aggregation.

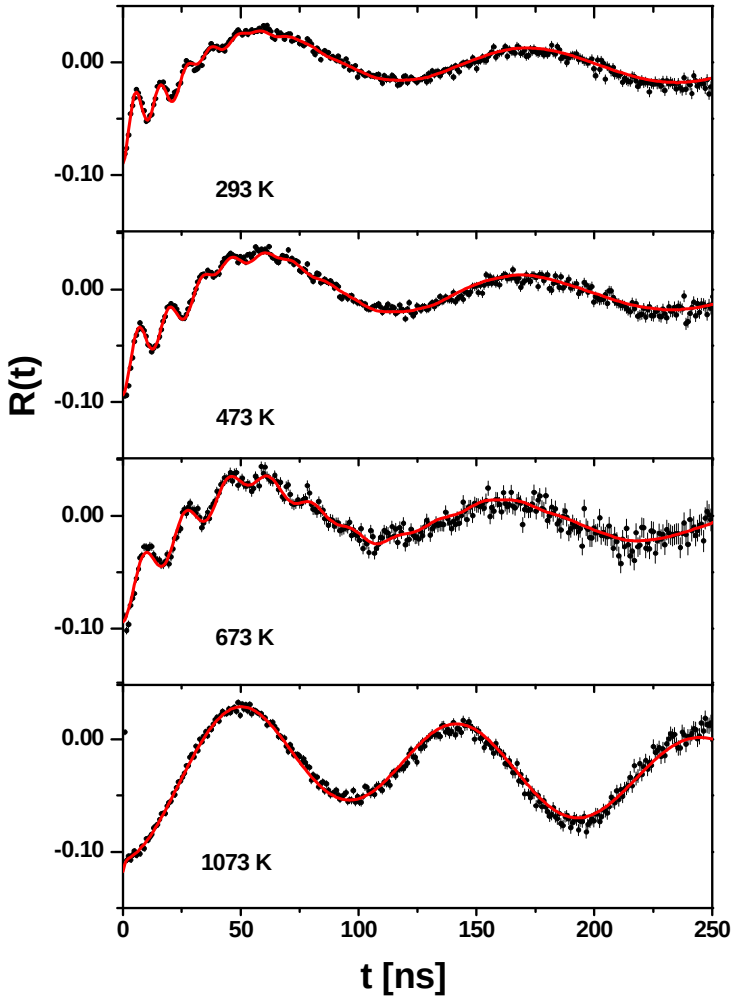

Fig. 1: Time dependent anisotropy of the ^{111}In 173 – 247 keV γ-γ cascade after implantation and annealing in AlN observed at different sample temperatures as indicated in the frames. The fast frequency is assigned to the ^{111}In-defect complex while the slower frequency is typical for the quadrupole interaction of undisturbed substitutional probes at the cation site.

2. Proposed work

2.1 Temperature dependent PAC measurements using ^{111m}Cd(^{111}Cd) and ^{117}Cd(^{117}In) and β–γ measurements using ^{115}Cd(^{115}In)

The PAC measurements presented above arose some questions which we aim to answer with this project:

a) The actual measurement with the ^{111}In(^{111}Cd) probe is performed using the γ–γ-cascade of the daughter nucleus ^{111}Cd. While In is isoelectronic to Ga and Al, Cd can act as an acceptor in GaN. This can significantly alter the interaction mechanisms of the probe element with defects. On the other hand, it is commonly believed that the decay times of the γ–γ-cascade are too fast to allow any re-arrangement of atoms or diffusion. So the observed complex and its dynamic behaviour, within the 300ns of the characteristic PAC analysing time window, will only be determined by the chemical and physical properties of In and not Cd. This assumption will be studied in this proposal by performing measurements with the PAC-probes ^{111m}Cd(^{111}Cd) and ^{117}Cd(^{117}In). If the trapping of the defect is due to the Cd-acceptor it should be visible in the measurements with the former probe while it is possible that the complex dissociates during the measurement with the latter probe. Previous measurements

showed that after implantation Cd impurities occupy the same site as the In probe[16,17]. However, the temperature dependence of the interaction was not studied in these investigations. The assumption, that the defect might be trapped by *any* oversized impurity due to strain fields around the probe can be dismissed, since no reversible behaviour was observed in temperature dependent PAC measurements using the ^{181}Hf(^{181}Ta) probe which has the same covalent radius as the In probe[18].

b) The second question that will be addressed is the role of "after effects" in the measurements with the ^{111}In(^{111}Cd) probe. Disturbances of the probe's electronic shell are caused by the decay of ^{111}In to ^{111}Cd via electron capture. The hole in the electron shell will be filled by x-ray and Auger processes leaving further holes and excited states that cause fluctuating field gradients. In some insulators, where the recombination processes are slow due to the low electron mobility, this was seen to cause the loss of angular correlation[19], however, in semiconductors usually the holes are filled in a short time interval within the time resolution of the spectrometer and therefore do not interfere with the measurement. The occurrence of "after effects" is dependent on the material, the availability of electrons, their mobility and the measuring temperature. In fact, preliminary measurements with ^{111}In(^{111}Cd) in AlN showed a damping of the fast defect frequency at low temperatures (< 150 K) which might be due to these effects. A detailed study of the influence of "after effects" will be possible by using the PAC probe ^{111m}Cd(^{111}Cd) and by comparing the results of a γ–γ to that of an e^-–γ PAC measurement. In both cases the same intermediate state is populated as for ^{111}In(^{111}Cd) but in the γ–γ case no holes are created in the electron shell.

c) Finally, the use of the probe ^{115}Cd(^{115}In) will allow the determination of the sign of the quadrupole interaction by means of a β–γ measurement. Although the half life of the intermediate state of this nucleus is much shorter than that of the comparable states in ^{111}Cd and ^{117}In, with the information gained by the studies suggested above, it should be possible to extract the necessary information. This would be very important since, at present, density functional calculations of the electric field gradient (EFG) in the nitride semiconductors are hampered by the fact that the value of the u-parameter (u=b/c where b is the bond-length in the c-direction and c the lattice parameter) is not known with sufficient precision neither in GaN nor in AlN. Variations of the u-parameter within the experimental errors cause even the sign of the numerical EFG result to change, rendering any calculations uncertain at present.

Detailed temperature dependent γ–γ-PAC measurements will be performed from 20 K up to 1200 K using ^{111m}Cd(^{111}Cd) and ^{117}Cd(^{117}In) as PAC probes. In the case of ^{117}Cd(^{117}In) the isotope ^{117}Ag will be implanted which decays into the proper state of ^{117}Cd with a half-life of 73 s. After the implantation samples will be annealed at 1000ºC to remove implantation damage and the measurements will be performed using a closed cycle He refrigerator for measurements below room temperature and a graphite heater PAC-oven for measurements at elevated temperatures under vacuum.

Complementary γ–γ and e^-–γ PAC measurements with the ^{111}Ag(^{111}Cd) probe will assess the incorporation of Ag in the crystal. This additional information can help to interpret the measurements where the actual PAC probes (^{115}Cd and ^{117}Cd) are incorporated by recoil implantation during the decay of the implanted isotopes ^{115}Ag and ^{117}Ag. Furthermore, those measurements are another test-case for the capability of large impurities to trap point defects.

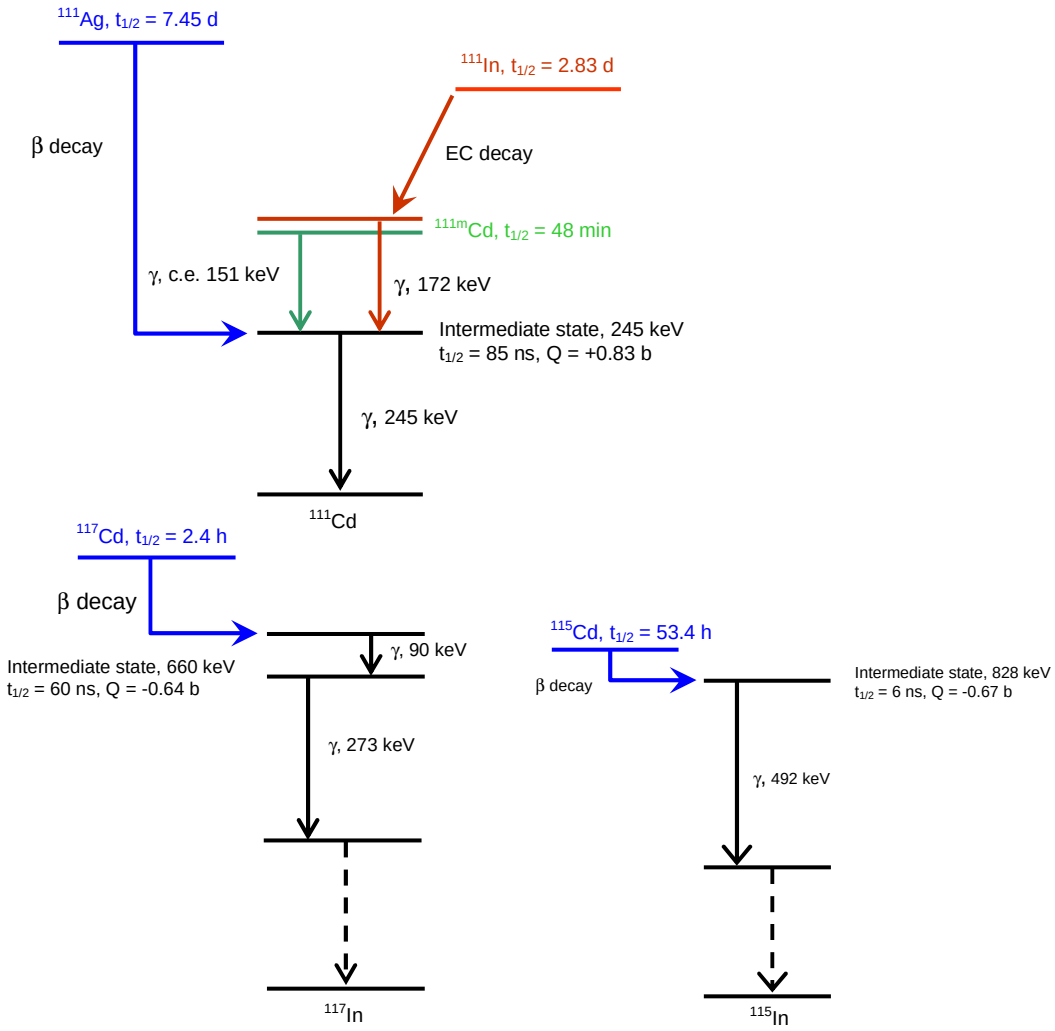

Fig. 2: Partial decay schemes of the five PAC-probes to be used in this proposal

2.2 Complementary measurements

Complementary experiments will be performed at the home institutions of the groups involved in this proposal. At ITN, Portugal, Rutherford Backscattering and channelling (RBS/C) measurements will be performed to assess the lattice site location of implanted stable In and Cd ions and the produced implantation damage. High resolution X-ray diffraction (XRD) analysis will be used to investigate the hydrostatic strain that is induced in the lattice by defects.

At Bonn university, Germany, PAC measurements will be performed using the probes ^{111}In(^{111}Cd) and ^{181}Hf(^{181}Ta) which can be implanted at the radioactive isotope separator BONIS[20].

Furthermore, pre-implantations of stable In and Cd will be performed which will act as competitive centre for V_N trapping during the PAC measurements. In fact, in a preliminary study using the PAC probe ^{111}In(^{111}Cd) and a pre-implantation of stable In, reduced trapping of V_N was observed at the radioactive ^{111}In probe indicating that available V_N have been trapped at the stable In ions.

3. Beam time request and experimental requirements at ISOLDE

We estimate the total amount of ISOLDE beam time needed to accomplish the above-described tasks to be 28 shifts within two years:

Table I: Beam time request

Required isotope	Implanted beam	PAC experiment	Intensity [at/μC]	Target / Ion source	Comments	nº of shifts
^{111m}Cd	^{111m}Cd	γ–γ, e^-–γ	10^8	molten Sn, plasma		16
^{117}Cd	^{117}Ag	γ–γ	10^8	UC_2, RILIS (Ag)	Nb or Ta ion source cavity to decrease In surface ionization contamination	8
^{115}Cd	^{115}Ag	β–γ	10^8			2
^{111}Ag	^{111}Ag	β–γ, γ–γ	5×10^7			2

Ag beam times are quite requested by other experiments and have been recently delivered in 2007. All of our beam times consist of collections to be measured off-line and can in this way be easily shared with other users. We stress the particular case of the ^{111m}Cd beam time, where collections should run day and night with a period of about 4-5 hours between collections that usually last for 15-30 min. There are actually four PAC setups co-shared during beam times and the samples can be implanted on the same collective sample holder used with other users which are also doing PAC experiments.

For these PAC experiments, the number of implanted atoms per sample range from $5\cdot10^8$ up to 10^{11}, depending on half-lives, coincidence efficiency and on the fluence limit for proper recovery of the implantation damage. All isotopes will be collected in the general-purpose implantation chambers at GLM and/or High Voltage Platform at the ISOLDE hall, building 170. All γ–γ PAC measurements will be performed off-line, outside the ISOLDE hall, in the new Solid State Laboratory in building 115.

e^-–γ PAC experiments are performed at the ISOLDE off-line laboratory, building 275, room R-011. Several furnace systems exist already at ISOLDE for annealing treatments under vacuum or gas flow at atmospheric pressure at the new SSP lab.

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