

## Incorporation of the Donor Indium in Nanocrystalline ZnO

TH. AGNE<sup>1</sup>), Z. GUAN, X. M. LI, H. WOLF, and TH. WICHERT

*Technische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany*

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Nanocrystalline zinc oxide (n-ZnO) doped with <sup>111</sup>In has been prepared by the method of electrochemical deposition under oxidizing conditions (EDOC). After growth, a crystal size of 5 nm was determined. Investigations of the incorporation of <sup>111</sup>In in the host lattice are performed by the method of perturbed  $\gamma\gamma$ -angular correlation (PAC). After growth, the PAC experiments show that <sup>111</sup>In is incorporated in a not yet identified complex local structure. Subsequent annealing at about 573 K incorporates <sup>111</sup>In on substitutional Zn site in n-ZnO, which is a prerequisite for the incorporation of In as a shallow donor.

**Introduction** Nanocrystalline semiconductors provide interesting materials for new applications in optoelectronic devices. For example, the bandgap of the nanocrystals can be designed by variation of the size of the crystallites. Additionally, the lifetime or the oscillator strength of the electron-hole recombination in nanocrystals can be modified by doping with impurity atoms working as donors or acceptors.

The incorporation of impurity atoms into the host lattice has been investigated by EXAFS studies on heavily doped nanoparticles [1, 2]. The EXAFS method provides an averaged information about the local environment of impurities and needs a dopant concentration of more than  $10^{18}$  cm<sup>-3</sup>. The method of perturbed  $\gamma\gamma$ -angular correlation (PAC) gives information about the local environment of the used probe atom and needs only a total number of  $10^{11}$  probe atoms corresponding to local concentration of typically  $10^{14}$ – $10^{16}$  cm<sup>-3</sup>. Therefore, one crystallite contains at most one PAC probe atom. The comprehensive understanding of the incorporation of impurities in low-level doped nanocrystals might be helpful for the preparation of nanocrystals with new optical properties.

The present PAC investigations yield conditions for the incorporation of <sup>111</sup>In in nanocrystalline ZnO on substitutional Zn sites, which is a prerequisite for the incorporation of <sup>111</sup>In as a shallow donor in this material.

**Sample Preparation** Nanocrystalline ZnO (n-ZnO) was produced by the EDOC method (Electrochemical Deposition under Oxidizing Conditions), which is based on the reduction of metal ions supplied by a sacrificial anode in a non-aqueous medium [3, 4]. The electrolysis takes place in a solution of 0.1 M tetrabutylammonium-bromide (TBA-Br) in 2-propanol. After growth of n-ZnO, TBA works as stabilizer by capping the colloidal nanocrystallites. For both electrodes, a zinc-foil with a purity of 99.9997% (Aldrich Chemical Company) was used. Before the growth, the zinc foil was rinsed in an ultrasonic bath in 2-propanol and in acetone, each for 5 min, and subsequently dried

<sup>1</sup>) Corresponding author; e-mail: Thomas.Agne@tech-phys.uni-sb.de

in a N<sub>2</sub>-gas stream. For the electrolysis a current density of 5 mA/cm<sup>2</sup> was applied, whereby the temperature slowly increased from 295 to 313 K. In some experiments, the TBA-cap of the nanocrystals was removed by washing the colloids after preparation in a solution of 50% diethyl ether and 50% ethyl alcohol.

The n-ZnO crystallites were doped *in situ* with <sup>111</sup>In by diffusing the <sup>111</sup>In dopants from a dried <sup>111</sup>InCl solution into the sacrificial electrode at 400 K for 60 min. By measuring the radioactivity of the produced n-ZnO (typically 60 mg) a relative concentration of 1 ppb was determined. Before <sup>111</sup>In diffusion, one sample was additionally doped with Cu by depositing a 20 nm Cu layer onto the sacrificial electrode and diffusing at 623 K for 17 h. In this case, the electrode was cleaned by plasma etching before the diffusion procedures. The Cu concentration was estimated to 50 ppm.

**Experimental Details** The PAC method has been established as a useful tool for the investigation of dopants in semiconductors [5]. For the present experiments, exclusively the isotope <sup>111</sup>In was used. The detected electric field gradient (EFG) is determined by the distribution of the local charge density and, therefore, characteristic for intrinsic or extrinsic defects, lattice relaxations, and the formation of precipitations.

The PAC technique is based on the hyperfine interaction of the quadrupole moment of a suitable radioactive probe (<sup>111</sup>In/<sup>111</sup>Cd) with the EFG caused by the surrounding charge distribution. The radioactive decay of <sup>111</sup>In implies a  $\gamma\gamma$  cascade populating the isomeric level of the daughter nucleus <sup>111</sup>Cd, which in ZnO is isoelectronic to the host atom Zn. The interaction between the quadrupole moment  $Q$  of the isomeric  $I = 5/2$  level of <sup>111</sup>Cd and the external EFG causes the observation of three frequencies  $\omega_1$ ,  $\omega_2$ , and  $\omega_3 = \omega_1 + \omega_2$  in the PAC time spectrum  $R(t)$ . The frequencies  $\omega_i$  are proportional to the largest component of the traceless EFG tensor ( $V_{zz}$ ), which is usually expressed by the quadrupole coupling constant  $\nu_Q = eQV_{zz}/h$ . The asymmetry parameter  $\eta = (V_{xx} - V_{yy})/V_{zz}$  is deduced from the frequency ratio  $\omega_2/\omega_1$  and satisfies the condition  $0 \leq \eta \leq 1$  ( $V_{zz} \geq V_{yy} \geq V_{xx}$ ). The frequencies  $\omega_i$  are directly visible in the Fourier transform  $F(\omega)$  whereby the actual fit is performed using the time spectrum  $R(t)$ . Besides  $\omega_i$ , it extracts the amplitudes of the frequencies  $\omega_i$  yielding information about the fraction of <sup>111</sup>In atoms that is associated with this EFG. A detailed description of the PAC spectroscopy is found e.g. in [5].

**Results and Discussion** After growth, X-ray diffraction (XRD) experiments were performed. They showed the presence of ZnO crystallites with a mean diameter of about 5 nm.

The PAC spectra measured after the growth of n-ZnO exhibit a broad frequency distribution indicating that the <sup>111</sup>In atoms are incorporated in non-unique crystalline environments. After annealing above 373 K the frequency distribution becomes smaller and is present up to an annealing temperature of 523 K. The extracted electric field gradient is characterized by  $\nu_Q \approx 130(10)$  MHz,  $\eta \approx 0.4$  (see Fig. 1a, EFG #1). Comparing this EFG with that of metallic Zn ( $\nu_Q = 133.1$  MHz,  $\eta = 0$  [6]), the coupling constant  $\nu_Q$  is similar, but the different asymmetry parameters do not support the interpretation in terms of <sup>111</sup>In atoms residing in Zn clusters, which may be present in case of an incomplete oxidation of Zn during the preparation process. The EFG measured in In<sub>2</sub>O<sub>3</sub> ( $\nu_Q = 155.2$  MHz,  $\eta = 0$  and  $\nu_Q = 119.1$  MHz,  $\eta = 0.71$  [7]) are also close to EFG #1, but the formation of separate <sup>111</sup>In<sub>2</sub>O<sub>3</sub> cluster is also excluded since a very

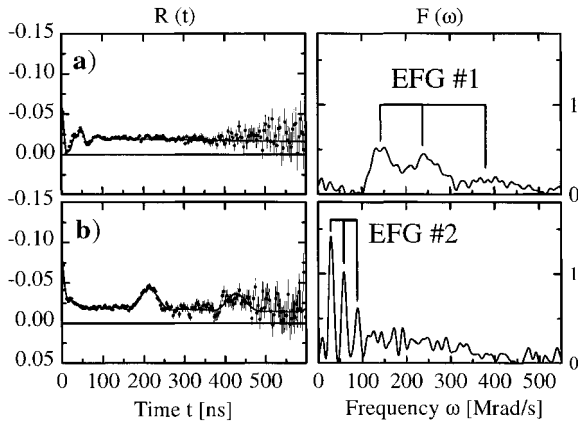


Fig. 1. PAC spectra of n-ZnO after annealing at a) 523 and b) 723 K

small quantity of radioactive  $^{111}\text{In}$  was used. The local lattice structure causing EFG #1, therefore, could not be identified until now.

After annealing above 573 K, a second EFG is observed with  $\nu_Q = 31.2(5)$  MHz,  $\eta = 0$  (see Fig. 1b, EFG #2). It is well-known from bulk ZnO and is caused by the hexagonal lattice structure ( $\nu_Q = 31.2(1)$  MHz,  $\eta = 0$  [8]). In bulk ZnO, the impurity In acts as a donor if it is incorporated on the Zn site. Because of the identical EFG, i.e. the identical local lattice environment of the  $^{111}\text{In}$  atoms, it is concluded that the In atoms described by EFG #2 are incorporated on Zn sites ( $\text{In}_{\text{Zn}}$ ) in n-ZnO and can act as donors.

After preparation the samples were encapsulated into quartz ampoules and annealed under different external conditions; the annealing time was 60 min in each case. The variation of the EFG parameters upon annealing will be discussed in the following.

Figure 2 shows the fraction of  $^{111}\text{In}$  atoms characterized by EFG #1 and EFG #2 as a function of temperature for different conditions of annealing.

In Fig. 2a, the n-ZnO sample was annealed without TBA-cap under oxygen atmosphere. The fraction of the unknown configuration (EFG #1) increases with increasing annealing temperature up to 573 K (for  $T_A = 523$  K see Fig. 1a). At this temperature EFG #2 corresponding to  $\text{In}_{\text{Zn}}$  atoms is visible for the first time and its fraction increases up to 24% at 773 K. At the same time the fraction of configuration (#1) decreases.

In Fig. 2b, n-ZnO was annealed with TBA-cap under oxygen atmosphere. The temperature dependence of both fractions is similar to the first case, but the maximum fraction of EFG #2 reaches only 15% at a higher temperature (above 698 K). Since the TBA-cap around the n-ZnO prevents the grain growth during annealing, a correlation between the incorporation of In on Zn sites and the crystal size seems to be unlikely.

In Fig. 2c, the nanocrystals were annealed without TBA-cap in vacuum. The EFG #2 is not observed below 623 K. The corresponding fraction increases up to 18% at 723 K (see also Fig. 1b), decreases at higher temperatures and vanishes completely at 873 K. At the same time the fraction of configuration (#1) changes only slightly. This observation indicates that the incorporation of In on Zn sites does not depend on an additional oxidation process during annealing in  $\text{O}_2$  atmosphere.

In Fig. 2d, the case of Cu-doped n-ZnO, the fraction of EFG #2 shows a significantly different behavior. After growth only the PAC signal of configuration EFG #2 is ob-

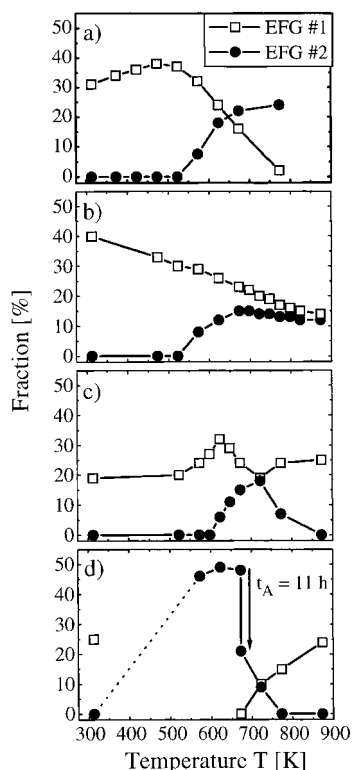


Fig. 2. Fractions of In atoms vs. temperature observed at different conditions of annealing: a) without TBA-cap in oxygen, b) with TBA-cap in oxygen, c) without TBA-cap in vacuum and d) doped with Cu and annealed without TBA-cap in oxygen

served. After annealing at 573 K (without cap under oxygen atmosphere), the fraction of EFG #2 amounts about 50% and remains constant up to 673 K. At this temperature the sample was annealed a second time, but now for 11 h. The fraction of EFG #2 is reduced to 21%, and, at the same time, the color of the sample changes from white to light yellow. Increasing the annealing temperature up to 773 K the fraction of EFG #2 vanishes completely and the yellow color of the sample becomes more intensive. In this sample the incorporation of  $^{111}\text{In}$  atoms on substitutional Zn sites was obviously more effective than in the other samples but, at present, this effect cannot be assigned to the co-doping with Cu in a unique way, since also the preparation route was changed. In contrast to previous PAC experiments in bulk ZnO [9], the formation of  $^{111}\text{In}$ -Cu pairs is not observed.

**Conclusion** The incorporation of the donor  $^{111}\text{In}$  in n-ZnO was investigated by the PAC method. After growth and up to an annealing temperature of typically 573 K, the PAC measurements show the In atoms incorporated in a not yet identified local lattice structure (EFG #1). At higher annealing temperatures the population of  $\text{In}_{\text{Zn}}$  sites is observed (EFG #2), which is a prerequisite for the incorporation of In as a shallow donor. The population of this site under different preparation and annealing conditions is shown.

The present experiments prove that the PAC method is a useful tool to investigate the incorporation of dopants in nanocrystalline semiconductors. In case of II-VI semiconductors available probe atoms are as donors  $^{111}\text{In}$  and  $^{77}\text{Br}$  and as acceptors  $^{111}\text{Ag}$  and  $^{73}\text{As}$ . Since the PAC method needs only  $10^{11}$ – $10^{12}$  atoms the incorporation of a single dopant in a nanocrystal can be excellently investigated.

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