Synthesis and local structure of doped nanocrystalline zinc oxides

Joachim U. Brehm^{a)}

*Joint Research Laboratory Nanomaterials, Technical University Darmstadt
and Forschungszentrum Karlsruhe, Petersenstrasse 23, 64287 Darmstadt, Germany*

Markus Winterer

*Institute of Combustion and Gasdynamics, University Duisburg-Essen, Lotharstrasse 1,
47057 Duisburg, Germany*

Horst Hahn

*Joint Research Laboratory Nanomaterials, Technical University Darmstadt
and Forschungszentrum Karlsruhe, Petersenstrasse 23, 64287 Darmstadt, Germany*

(Received 28 February 2006; accepted 22 June 2006; published online 25 September 2006)

Nanocrystalline zinc oxides are produced by chemical vapor synthesis and characterized by x-ray diffraction, high resolution transmission electron microscopy, nitrogen sorption, and extended x-ray absorption fine structure. Dopant elements (aluminum, gallium, and indium) influence the particle size of the powders as well as lattice parameters and local structure. The different effects of the three dopant elements are characterized. © 2006 American Institute of Physics.

[DOI: [10.1063/1.2349430](https://doi.org/10.1063/1.2349430)]

I. INTRODUCTION

Semiconducting transparent thin films of oxide materials have been known since the discovery of conducting cadmium oxide by Badeker in 1907.¹ About 50 years later with the deposition of tin-doped indium oxide (known as ITO or indium-tin oxide) films the class of transparent conducting oxides (TCOs) was coined. These materials mostly find applications as thin films, for example, in flat panel displays, low-emissivity windows, solar cells, transparent heating elements in windscreens, gas sensors, and antistatic coatings. TCO films are commonly prepared by physical- or chemical-vapor-deposition-type processes with their well known advantages. An overview on the preparation and applications of TCOs can be found in Ref. 2. Most of these preparation techniques require high substrate temperatures. Alternative methods of applying a film are required for substrate materials with low melting points such as polymers. Therefore, nanocrystalline dispersible particles are of interest. Today ITO is the most commonly used material in industrial applications. Because of the rare abundance and consequently high price of indium in nature, materials with similar properties and higher availability are sought after.

One promising replacement material is doped zinc oxide. In the production of solar cells it has already replaced ITO due to its higher resistance to deterioration in plasma involving processes. We produced group-III-doped ZnO by chemical vapor synthesis³ (CVS) at atmospheric pressures. The position of dopants in the host lattice is of major importance for properties such as conductivity.⁴ In order to understand the influence of dopants on structure and properties, the samples were characterized by x-ray diffraction, high resolution transmission electron microscopy, nitrogen sorption, and extended x-ray absorption fine structure (EXAFS). Up to now EXAFS investigations of ZnO mainly concern topics of

structural development in pure ZnO (Refs. 5–7 or the use of Cu-doped ZnO for catalysis of methanol synthesis.^{8–10} Only two investigations exist on In-doped ZnO analyzed by EXAFS.^{11,12}

II. EXPERIMENTAL METHODOLOGY

Nanocrystalline zinc oxide was synthesized using zinc-tetramethyl-heptanedionate ($\text{Zn}(\text{thd})_2$) as solid precursor (Epichem Oxides & Nitrides, Mildenhall, U.K.) and aluminum-, gallium-, and indium-tetramethyl-heptanedionate for doping. Figure 1 shows a schematic drawing of the experimental setup of the reactor. Helium [400 SCCM (SCCM denotes cubic centimeter per minute at STP)] is used to transport the precursor vapor to the reaction zone, and oxygen (5000 SCCM) is added well behind the precursor container to prevent preliminary oxidation and/or combustion. The precursor vapor is transported into the hot wall reactor where it decomposes and reacts to oxide particles which grow by collision and sintering to nanometer sized particles. These are transported by the gas stream to the particle collector, where they are separated from the gas stream by thermophoresis through a thermal gradient between infrared lamps and the water cooled walls. Furnace temperatures of 1000 °C and atmospheric pressure were used as process parameters with resulting residence times in the hot zone of about 0.3 s.

Characterization of the powders was performed using a nitrogen sorption instrument Autosorb 3B (Quantachrome) to determine the specific surface area. The powders were heated to 200 °C under vacuum before the sorption measurements to remove adsorbed molecules from the sample surface. Transmission electron microscopy by a CM20 Ultra Twin (Philips) was employed to determine crystallinity and grain size distribution. Crystalline phases, crystallite sizes, and lattice parameters were determined by x-ray diffraction (XRD) at room temperature using an x-ray diffractometer D-5000

^{a)}Electronic mail: joachim_brehm@web.de

FIG. 1. (Color online) Experimental setup of the CVS system for the production of nanocrystalline ZnO and doped ZnO (T_1 was about 200–220 °C and T_2 1000 °C).

(Siemens). Primary particle sizes (corresponding to coherent diffracting domains) were calculated from the line broadening using Rietveld refinements by FULLPROF (Ref. 13) of Cu $K\alpha$ XRD patterns. The local structure was determined by EXAFS measured at Zn K edge (9659 eV), In K edge (27 940 eV), and Ga K edge (10 367 eV) in transmission at HASYLAB (DESY, Hamburg) beamlines A1 and X1 at room temperature. EXAFS data were measured up to 1000 eV above the K -edge energies except for samples doped with Ga due to overlap of the Zn- K -edge data with those of the Ga K edge. For sample preparation appropriate amounts of the nanocrystalline powders were mixed in a mortar with polyethylene (spectrophotometric grade, Aldrich) and then uniaxially pressed at 250 MPa pressure to yield pellets of 12 mm diameter and approximately 0.7 mm thickness. The dopant- K -edge measurements were repeated four times to improve the signal-to-noise ratio since the content of dopants was low. After extracting the data for the Zn- K -edge measurement, the dopant- K -edge measurements were averaged and then the EXAFS data were also extracted. The dopant content was determined by analysis of the absorption coefficient. The results agree with the nominally intended dopant content for Ga and In doping (see Table I); for Al doping no data are available.

III. DATA ANALYSIS

In Rietveld refinements of powder diffraction patterns the complete diffractogram is fitted by a nonlinear least-

squares method using a structure factor computed from the appropriate space group and coordinates of the asymmetric unit. XRD Rietveld refinements were performed with FULLPROF using initial values for the wurtzite ZnO structure (space group 186, $P6_3mc$) published by Albertson *et al.*¹⁴ Analysis of the isotropic microstrain and grain size broadening is possible using a Thompson-Cox-Hastings-pseudo-Voigt line shape function. Errors were estimated using standard FULLPROF procedures. The background was refined using a polynomial function.

The EXAFS signal $\chi_i(k)$ of the absorbing atom type i can be computed by a product integral of the partial pair distribution functions of all scattering atoms j with the EXAFS signal corresponding to a single pair of atoms $\gamma_{ij}(r, k)$ if only single scattering contributions are considered:

$$\chi_i(k) = \sum_j \int_0^\infty 4\pi r^2 \rho \gamma_{ij}(r, k) g_{ij}(r) dr, \quad (1)$$

where r is the distance from atom i and ρ is the number density of the sample. The EXAFS signal of an atom pair $\gamma_{ij}(r, k)$ is amplitude $[A_{ij}(k, r)]$ and phase $[\Phi_{ij}(k, r)]$ modulated:

$$\gamma_{ij}(r, k) = A_{ij}(k, r) \sin[2kr + \Phi_{ij}(k, r)]. \quad (2)$$

In order to eliminate multiple scattering observed for wurtzite-type structures, the data were filtered using a range up to 4 Å of the Fourier transform (FT) EXAFS spectra. Subsequently they were analyzed by a reverse Monte Carlo

TABLE I. Showcase results of Rietveld refinements used as input for RMCXAS simulations.

	Sample								
	ZnO			ZnO:In 5%			ZnO:Al 5%		
Z	2			2			2		
a, b (Å)	3.2516(2)			3.2581(5)			3.256(2)		
c (Å)	5.2096(4)			5.2123(9)			5.197(2)		
V (Å ³)	47.69(4)			47.9(2)			47.7(3)		
	x	y	z	x	y	z	x	y	z
Zn (dopant)	0.333	0.666	0.000	0.333	0.666	0.000	0.333	0.666	0.000
O	0.333	0.666	0.38(2)	0.333	0.666	0.39(2)	0.333	0.666	0.40(5)
X	0.16(4)			0.68(11)			1.24(36)		
Y	0.255(1)			0.377(5)			0.503(6)		
R_B (%)	1.64			2.82			3.84		
R_{wp} (%)	9.37			8.48			13.60		

TABLE II. Results of BET and XRD size determination (varying values due to sample variations, e.g., doping concentration) for different CVS nanocrystalline ZnO samples.

Sample (intended doping)	Method			
	BET Surface area (m ² /g)	BET Particle size (nm)	XRD Grain size (nm)	Dopant content (at. %)
ZnO	39	27.5(3)	25.2(4)	
ZnO:In 1%	33	32.5(3)	21.2(4)	
ZnO:In 5%	39	27.4(3)	14.9(3)	4.8(8)
ZnO:Ga 2%	36	30.0(3)	19.3(4)	2.1(3)
ZnO:Ga 3%	34	31.8(3)	17.8(4)	2.8(4)
ZnO:Al 2%			13.3(6)	
ZnO:Al 5%	56	19.0(2)	11.1(4)	

(RMC) based method by the RMCXAS program in k space as described in Ref. 15. The amplitude and phase functions for this configuration were calculated using FEFF8 (Ref. 16) neglecting multiple scattering by only calculating second order distribution functions. The RMCXAS program was run with configurations of 784 atoms (containing appropriate amounts of dopant atoms) and appropriate hard-sphere potentials for the different models. The size of the box of atoms was four times the lattice constant c and seven times the a and b lattice constants using lattice parameters obtained by Rietveld refinement of XRD data (see Table II). A constant error of $\sigma_i=0.003$ representing the “temperature” was used for all RMC fits. After a sufficient number of cycles (typically the number of cycles equals the number of atoms) convergence was obtained.

With RMCXAS two spectra with the structural information from two different x-ray absorbing elements in the sample can be fitted simultaneously with one mutual model. The deviation between the fitted model and the measurement is indicated by the so called R value and is given in percent. It is possible to extract partial pair distribution functions for Zn–Zn and Zn–O from a single Zn- K -edge spectra because the EXAFS signal depends on the backscattering atoms by phase and amplitude functions. The partial pair distribution functions obtained by RMC were analyzed by a moment analysis to yield coordination numbers, coordination distances, second moments, and corresponding errors.

IV. RESULTS AND DISCUSSION

A. Powder characterization

A typical transmission electron microscopy (TEM) micrograph (Fig. 2) of an In-doped ZnO sample shows that the crystallinity of the samples is very good. The lattice fringes extend across the total grain diameter up to the particle edges. This is due to the high synthesis temperatures. In this temperature regime solid state and surface diffusion are facilitated and defects can anneal during synthesis. The geometric mean deviation of the size distribution was in the range of 1.2–1.4. The morphology of the powders was mostly spherical with some grains showing hexagonal facets. No separate phases for doped samples can be observed by

FIG. 2. TEM image of In-doped ZnO.

electron diffraction. This is consistent with the low background between the Bragg reflections observed in XRD patterns. Sintering necks are rarely observed at the particle contacts. Measurements by nitrogen sorption revealed high surface areas of 32–56 m²/g for the powders produced by atmospheric pressure CVS (see Table II). Average particle sizes were calculated from the specific surface area assuming

FIG. 3. X-ray diffractograms of the synthesized powders (top, comparison of Al-doped and undoped ZnO; bottom, Rietveld refinement of In-doped ZnO).

TABLE III. Ionic radii for different coordinations of the cations in the different samples (Ref. 28).

Cation type	Radius (pm) (four fold coordination)	Radius (pm) (Six fold coordination)
Zn (2 ⁺)	74	88
Al (3 ⁺)	53	68
Ga (3 ⁺)	61	76
In (3 ⁺)	76	94

separate, monodisperse, spherical particles. The grain size varies depending on the choice and amount of doping element from 10 to 25 nm (compare Fig. 3). Values of the isotropic particle size broadening are listed in Table II. The deviations between particle sizes determined from the specific surface area and the grain sizes determined by XRD are most probably due to the assumption of spherical particles and a small amount of agglomeration in the powders. The deviations between particle size and grain size are small for the pure ZnO samples. However, for the doped powders the grain size is considerably smaller compared to the particle size. This can be explained by a reduction of the sintering rate due to incorporation of the group III atoms into the ZnO lattice in the CVS process. In agreement with this explanation is the observation that the grain size is decreasing with increasing deviation of the dopant cationic radii from the ionic radius of zinc, implying different solid state diffusion coefficients. The CVS process consists of several parts: conversion of the precursor into monomers, formation of clusters from monomers, coagulation of clusters and formation of agglomerates, sintering of the primary particles within the agglomerates, and heat exchange with the reactor.¹⁷

B. Crystal structure: Lattice parameters

XRD patterns of the powder samples show only reflections of pure hexagonal wurtzite structure (space group: $P6_3mc$) for all ZnO samples prepared (see Rietveld refinement for ZnO:In in Fig. 3). The ionic radii for the possible four- or sixfold coordination for the cations are shown in

FIG. 4. Lattice parameter c as a function of dopant concentration from Rietveld refinements. FIG. 5. Lattice parameters a and b as a function of dopant concentration from Rietveld refinements.

Table III. Upon doping the lattice constants of the wurtzite structure change. The lattice parameter c decreases for dopant atoms with smaller ionic radii (Al and Ga) and increases with larger ionic radii (In) compared to Zn on which site the dopants are assumed to reside. The behavior of these changes can be seen in Fig. 4. The Ga- and In-doped samples show an approximately linear change with concentration. A deviation from this is observed for the sample doped with 2 at. % Al since it does not show a smaller value compared to the 2 at. % Ga-doped sample.

The following effects are found for the a and b lattice constants of the hexagonal plane: substitution by the larger In atoms increases lattice parameters a and b due to the larger ionic radius in agreement with the linear Vegard's law. For Al and Ga a surprising behavior is observed. Both ions are smaller than Zn, yet larger values for a and b are found, which cannot be explained geometrically by atoms of Al and Ga residing on Zn lattice sites (Fig. 5). Again Ga doping shows a linear behavior with increasing dopant level whereas for Al a nonlinear behavior is observed. The unit cell volume can be calculated from the lattice parameters. Surprisingly, for all samples the unit cell volume also increases with increasing dopant content (Fig. 6). The increase of the unit cell volume correlates with the ionic radii: for In the effect is

FIG. 6. Lattice volume as a function of dopant concentration from Rietveld refinements.

FIG. 7. Microstrain depending as a function of dopant concentration from Rietveld refinements.

largest, while for Al the effect is smallest. The microstrain obtained from the Rietveld refinement increases linearly with dopant concentration and is largest for Al (Fig. 7), correlating to the highest difference in ionic radius between dopant and zinc ions. So the effects on the cell structure are influenced by the differences of ionic radii of the dopants and their concentration.

The changes in lattice parameters cannot be sufficiently understood by taking only ionic radii into account. Another possible explanation is the general change of lattice parameters in covalent systems with decreasing grain size. It has been shown^{18,19} that in nanocrystalline systems a relaxation of lattice parameters due to a decrease of the integral attractive forces in the crystal occurs. This can explain the observation of increasing a and b lattice parameters independent of the type of dopant. Considering a softer bond between Zn and O in the c direction (see the next section), it is clear that this lattice parameter is much more sensitive on the type of dopant element. The higher charge density of the dopant elements of group III compared to Zn^{2+} leads to high attractive forces between substitutional dopant atoms and oxygen neighbors along the c axis. Therefore, the c parameter shows a strong dependence on dopant element size and charge density.

C. Crystal structure: Parameter u and bond length

In the ZnO wurtzite structure zinc atoms occupy the special position $1/3, 2/3, 0$ and oxygen occupies the special position $1/3, 2/3, u$. Therefore, u can be interpreted as the relative shift of the anionic sublattice to the cationic sublattice in z direction. In the literature^{7,8} values for u of 0.3817–0.3819 are found. Kisi and Elcombe²⁰ present a correlation $u(c/a) = \sqrt{3}/8$ for u with the lattice parameter ratio c/a derived from geometrical considerations on the basis of a hexagonal close packing. They present values of own measurements and literature values of differently prepared ZnS and ZnO samples. In Fig. 8 the straight line represents this correlation. The data points represent the results of the differently doped and also the pure nanocrystalline ZnO investigated here. The decrease of c/a with larger u is much less pronounced for our samples compared to Kisi and Elcombe's

FIG. 8. Ratio of lattice parameters c/a as a function of position parameter u compared to the relation found by Kisi and Elcombe. The error bars are smaller than the symbol size.

results. Similar results have been published²¹ for one sample of nanocrystalline ZnO indicating a dependence of the $c/a - u$ correlation on the reactants used in the used wet chemical synthesis. The ratio c/a as a function of dopant concentration (Fig. 9) decreases generally with increasing dopant content.

The decrease of c/a has also been observed in structural investigations of the wurtzite to rocksalt transformation in high-pressure experiments.²² Therefore, the behavior in our samples may be interpreted by an internal pressure induced by the dopants. An alternative explanation for this behavior can also be internal strain as observed by the general increase in microstrain with increasing dopant content in the Rietveld results.

From the values of u further insight into the structure can be obtained. Only in an ideal wurtzite crystal structure with $c/a = 1.6333$ and $u = 3/8$ all Zn–O bond lengths are identical. For deviations in c/a and u the Zn–O bond in the c -axis direction is different in comparison with the other Zn–O bond lengths. The bond length in the c direction can simply be calculated by uc and the other three by $[a^2/3 + (1/2 - u)^2 c^2]^{1/2}$ (Table IV). The bond lengths parallel to the a, b

FIG. 9. c/a ratio as a function of doping level.

TABLE IV. Bond length for Zn–O determined from Rietveld refined parameters.

Sample	Distances $\perp c$ r (Å)	Distance $\parallel c$ r (Å)
Ideal wurtzite	1.98	1.98
ZnO	1.97(2)	2.00(2)
ZnO:Al 5%	1.95(2)	2.08(2)
ZnO:Ga 3%	1.96(2)	2.04(2)
ZnO:In 5%	1.97(2)	2.04(2)

plane remain nearly constant, whereas the Zn–O distance along the c axis increases according to the uc dependence. With decreasing values of c this can be interpreted by an internal pressure or higher strain in the particle. In high-pressure experiments similar behaviors for bond lengths and lattice parameters have been observed.

D. Local structure and dopant sites by extended x-ray absorption fine structure (EXAFS)

XRD provides only information averaged over the entire sampled volume on the basis of the long range order (periodic structure). As details of the local structure cannot be obtained by XRD, EXAFS was used to investigate whether the dopants are substitutional on Zn sites or reside on interstitial sites in the wurtzite crystal structure or form a second phase. Zn- K -edge and In- K -edge EXAFS spectra of ZnO doped with 5 at. % In were analyzed using RMCXAS with a single model (Fig. 10 and 11). The R values were 14% and 22% for Zn K edge and In K edge, respectively. The residuals in the optical Fourier transforms on both spectra have similar origin. The deviations at low radii are due to insufficient background subtraction. The deviation at about 4 Å arises from the cutoff in the pair distribution functions used to accommodate the Fourier filtering range in the RMC model. The remaining differences are probably due to multiple scattering.

The resulting partial pair distribution functions are shown in Fig. 12. They are normalized to the relative content of the absorbing element concentration in the samples. Therefore, In–O and Zn–O exhibit similar areas of the peaks. The In–In pair distribution is noisy due to the low In content. The average In–In distances are identical to the Zn–Zn distances. This is consistent with In substituting Zn since the distances of Zn to an interstitial cation would be much smaller as can be seen later. The In–O distances are shifted to higher values in comparison with Zn–O distances, reflecting the larger ionic radius of In. This information is not accessible from Rietveld analysis of XRD data as a periodic model is used. In Rietveld analysis this phenomenon can give rise to the observed behavior of microstrain. Coordination numbers, coordination distances, and second moments (corresponding to Debye-Waller factors) are displayed in Table V. It can be clearly seen that In has the same oxygen coordination number of 4 as Zn in contrast to pure In_2O_3 where the coordination number is 6. The In–O bond (2.08 Å) is longer compared to the Zn–O bond length (1.98 Å) due to the larger ionic radius of In. In pure bixbyite-type In_2O_3 it is

FIG. 10. RMC analysis of EXAFS spectra of In-doped (5 at. %) ZnO: Zn K edge on the top and optical Fourier transform on the bottom.

even longer with 2.17 Å.¹¹ These results agree with values for valence bonds computed from the bond lengths of In–O using the program BOND VALENCE CALCULATOR.²³ Values of 0.586 for In–O in our samples and 0.472 for In–O in pure In_2O_3 were obtained. These results reflect the stronger In–O binding due to less oxygen atoms available in comparison with the parent oxide and a higher charge density at In compared to Zn (note that bond valence values for Zn–O are also 0.472). For higher In contents the results in Ref. 11 show a sixfold coordination. For In contents comparable to our samples in Ref. 12 the same In–O distance and fourfold coordination were found. However, the error in coordination numbers from our analysis is smaller and, therefore, a coordination number of 6 can be excluded, in contrast to Ref. 12. Furthermore, the 12-fold Zn-cation next nearest neighbor coordination remains intact because the additional Zn–In contribution is included.

An extension of Vegard's law is the virtual crystal approximation (VCA). This theorem states that a linear change of the lattice parameter with dopant concentration results in a linear variation of the interatomic distances. The behavior of the cation-anion distance according to EXAFS for our samples is shown in Fig. 13. The VCA-like behavior is shown as a straight line calculated from Rietveld results. The Zn–O distances follow the VCA within the errors; nevertheless a behavior as presented in Ref. 24 with a dependence of

FIG. 11. RMC analysis of EXAFS spectra of In-doped (5 at. %) ZnO: In K edge on the top and optical Fourier transform on the bottom.

interatomic distances smaller than predicted by the VCA as a function of the composition seems possible. The In–O distances are definitely not following the VCA, showing a much larger distance at 5 at. % In than expected. Obviously, the In–O distances depend little on the composition in contrast to the VCA prediction. For the Zn–Zn distances a similar behavior as for Zn–O can be observed; however, a behavior

FIG. 12. Partial pair distribution function for (5 at. %) In-doped ZnO obtained by simultaneous RMC analysis of In- and Zn K edge EXAFS spectra.

with nearly constant values cannot be ruled out. Also for the Zn–In distances there is good overlapping with VCA in contrast to In–O. Therefore, we propose that the deformation of the nearest neighbors around the In atoms does not extend to the next nearest neighbors. There has to be some kind of relaxation, for example, adjusting bond angles rather than bond distances, as In–O distances do not follow the VCA prediction. Our observations are in contrast to the results on other samples [$\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ (Ref. 25)] where nearly constant cation-anion and cation-cation distances are found covering large compositional ranges. The VCA-like behavior of In^{3+} in ZnO is related to the oxygen in the samples investigated here, with much higher electronegativity in comparison with higher chalcogenides. Therefore, the bonds are more ionic and the cation-anion distances in ZnO react much more sensitive on doping than ZnSe or CdTe. This is due to the fact that the charge density at Mn^{2+} in ZnSe is lower in comparison with In^{3+} in ZnO.

A variety of initial configurations (with In on four- and sixfold interstitial sites) was used in the RMC analysis to verify the substitution of Zn by In. The four- and sixfold positions are the only available interstitial sites.²⁶ The resulting R values were $\sim 1000\%$ for fourfold interstitials and 50% for sixfold interstitials. Therefore, it is concluded that these models are unlikely for our samples. Another possible scenario is the formation of a separate In_2O_3 phase. This seems rather unlikely since there is no indication in XRD for a second phase in the sample and the observed change of the lattice parameters according to Vegard's law. Nevertheless, due to the small amount of In it might not show in XRD. Therefore, a corresponding model was run as RMC fit. Results of Rietveld refinements of pure In_2O_3 were used for the initial configuration of the second phase. The R values were 16% and 60% for Zn K edge and In K edge, respectively. It is obvious that this fit is worse compared to the model for In on Zn sites. Therefore, based on all results of XRD, EXAFS, VCA, and bond valence calculations it is concluded that In is located on substitutional Zn lattice sites and not on interstitial positions or as a separate phase of In_2O_3 . These conclusions are in agreement with the results for nanocrystalline samples published in Ref. 27.

The coordination number of oxygen neighbors for Zn is 3.0 (1.1) up to a distance of 2.3 Å which is just below the value for the distance in the c direction. This agrees well with the results from the Rietveld analysis, indicating a splitting of Zn–O bond lengths; nevertheless they were not conclusive since the In–O distances are also contained in the information from XRD.¹⁷ RMC analysis with high resolutions of 0.01 Å showed even stronger indications for the splitting of bond lengths as can be seen in Fig. 14 for an undoped ZnO sample.

The fits of the EXAFS spectra of Ga-doped samples were performed as described above. For Ga-doped ZnO samples the analysis is more complicated as the atomic numbers of Zn and Ga differ by only 1, resulting in a distance between K edges of $\Delta E \sim 700$ eV. Consequently, only the Zn- K -edge EXAFS data could be used from which only backscattering information on Ga is available. An R value of 11% for the Zn K edge was obtained for the assumption of

TABLE V. Coordination numbers, coordination distances, and second moments for In-doped ZnO determined by moment analysis of partial pair distribution functions determined by RMC analysis of EXAFS spectra.

Sample	Absorber/ scatterer pair	Coordination number N	Distance r (Å)	Second moment σ^2 (Å ²)	Edge measured
ZnO:In	Zn–O	3.9 (5)	1.98 (2)	0.007 (2)	ZnK+InK
ZnO:In	In–O	4.0 (4)	2.11 (1)	0.005 (2)	ZnK+InK
ZnO:In	Zn–Zn	10.9 (10)	3.23 (1)	0.012 (2)	ZnK+InK
ZnO:In	Zn–In	1.1 (17)	3.24 (1)	0.023 (2)	ZnK+InK
ZnO:In	In–In	0.9 (6)	3.21 (5)	0.004 (3)	ZnK+InK
ZnO:Ga	Zn–O	3.9 (5)	1.98 (1)	0.007 (2)	ZnK
ZnO:Ga	Zn–Zn	11.8 (16)	3.24 (1)	0.005 (1)	ZnK
ZnO:Ga	Zn–Ga	0.2 (2)	1.98 (1)	0.003 (1)	ZnK
ZnO:Al	Zn–O	4.0 (8)	1.98 (2)	0.008 (4)	ZnK
ZnO:Al	Zn–Zn	11.9 (23)	3.23 (1)	0.014 (5)	ZnK
ZnO:Al	Zn–Al	0.2 (3)	1.93 (5)	0.038 (13)	ZnK

substitutional Ga. For a model with interstitial Ga atoms a value of 10% could be achieved. For a fit without any Ga atoms an R value of 13% was achieved. Significant difference between the substitutional and interstitial models is not observed and no conclusion on the location of dopants is possible. In contrast to Al doping the backscattering information of Ga atoms is less conclusive because of the close vicinity of Zn and Ga in the periodic system. Therefore, the

backscattering amplitudes and phase functions of the two elements are very similar. The RMC results hint that Ga ions reside on interstitial sites.

For the Al-doped samples no Al- K -edge data were available because of the low energy of the Al K absorption edge. Therefore, only backscattering information for Al in Zn EXAFS experiments is accessible. Good fits with and without Al atoms could be obtained (an R value of 14% with Al on Zn sites and an R value of 15% without Al). In the pair distribution function of the model with substitutional Al a splitting of the first Al peak is observed. This is an indication for Al located not on substitutional but interstitial sites. For Al on sixfold and fourfold interstitial sites R values of 13% and 17%, respectively, resulted after convergence. From these results it seems as if Al resides on the sixfold interstitial site. A separate phase is unlikely, since the change of lattice constants in ZnO suggests an incorporation of dopant atoms and no indication of an aluminum oxide is found in XRD. A sketch of four- and sixfold interstitial sites in the wurtzite structure is shown in Fig. 15. The radius ratio rule²⁸ states that certain coordination numbers of anions around a cation are observed when the ratio of the ionic radii of cation to anion is larger than an empirically determined value. The minimum value of the radius ratio for octahedrally coordinated (interstitial) dopant ions in wurtzite is 0.414 (note that

FIG. 13. Cation-anion (top) and cation-cation (bottom) distances for In-doped samples according to EXAFS/RMC results. The dashed lines are calculated from Rietveld results and indicate the behavior suggested by VCA.

FIG. 14. Fit of bond lengths of pair distribution function of Zn–O bonds with a resolution of 0.01 Å.

FIG. 15. (Color online) sixfold interstitial site (white) and fourfold interstitial site (black) in the wurtzite ZnO structure. The large spheres represent O atoms, while light gray spheres represent Zn atoms.

for tetrahedral coordination the minimum value is 0.225); therefore, the sixfold coordination is possible for Al in this structure.

Together with the results from XRD presented in Table IV a difference for sixfold coordinated Al and Ga can be seen; the bond distances parallel to the hexagonal plane decrease slightly for these dopants whereas the bond distances in the z direction increase, reflecting again the possibly larger internal pressure or microstrain in the particles. Also a selective concentration at the surface as described in Ref. 29 could be explained; nevertheless this kind of concentration gradient is usually not observed in powders synthesized by CVS. The larger strain in the particles with higher dopant concentrations is also due to the smaller grain size (see Ref. 30 for grain size dependent strain results in undoped ZnO).

V. SUMMARY AND CONCLUSIONS

Nanocrystalline ZnO powders were produced by atmospheric pressure CVS. The grain size depends on type and amount of doped group III atoms. Only In- and Ga-doped samples followed Vegard's law. Al-doped samples behave significantly different. In atoms clearly reside substitutionally on Zn lattice sites. They show a larger distance to their next oxygen neighbors compared to Zn atoms, but the value is significantly lower than in pure indium oxide. This can be understood by the larger ionic radius and the higher charge density of In atoms in comparison with Zn. Due to an increase of the parameter u an increase of one Zn–O bond is observed by XRD and verified by EXAFS. The In atoms also exhibit a fourfold oxygen coordination just like the zinc atoms. The results suggest that Ga resides on interstitial sites like Al. The local structure around Ga atoms seems to be more distorted compared to the In-doped samples. The anomalous change of lattice parameters for Al-doped samples can be understood using the parameter u obtained by Rietveld analysis. The parameter u representing the relative

position of the anion sublattice is much larger than for the other dopants. Increasing u means a softer Zn–O bond along the c -axis direction. Therefore, a large decrease of the lattice parameter c is observed. The local structure around dopant atoms by EXAFS measurements with subsequent RMC analysis indicates a sixfold coordination of Al atoms. Future work will be done on NMR analysis of Al-doped samples.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support by the Federal Ministry of Education and Research (BMBF) through Project No. 03N4018. The XAFS measurements have been performed at the HASYLAB at DESY in Hamburg. The authors thank the staff of the A1 and X1 beamlines, particularly Edmund Welter, for their help.

- ¹K. Badeker, *Ann. Phys.* **22**, 749 (1907).
- ²H. L. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish, *Semiconducting Transparent Thin Films* (IOP, London, 1995).
- ³S. Klein, M. Winterer, and H. Hahn, *Chem. Vap. Deposition* **4**, 143 (1998).
- ⁴K. Ellmer, *J. Phys. D* **34**, 3097 (2001).
- ⁵F. Decremps, F. Datchi, A. M. Saitta, J. P. Itié, A. Polian, F. Baudelet, and S. Pascarelli, *High Press. Res.* **22**, 365 (2002).
- ⁶M. S. Tokumoto, S. H. Pulcinelli, C. V. Santilli, and V. Briois, *J. Phys. Chem. B* **107**, 568 (2003).
- ⁷E. M. Bachari, G. Baud, S. Ben Amor, and M. Jacquet, *Thin Solid Films* **348**, 165 (1999).
- ⁸C. Kiener, M. Kurtz, H. Wilmer, C. Hoffmann, H. W. Schmidt, J.-D. Grunwaldt, M. Muhler, and F. Schüth, *J. Catal.* **216**, 110 (2003).
- ⁹R. M. Friedman, J. J. Freeman, P. A. Berger, and F. W. Lytle, *Bull. Am. Phys. Soc.* **22**, 319 (1977).
- ¹⁰G. Vlaic, J. C. J. Bart, W. Cavignolo, N. Pianzolo, and S. Mobilio, *J. Catal.* **96**, 314 (1985).
- ¹¹T. Moriga, A. Fukushima, Y. Tominari, S. Hosokawa, I. Nakabayashi, and K. Tominaga, *J. Synchrotron Radiat.* **8**, 785 (2001).
- ¹²M. S. Tokumoto, A. Smith, C. V. Santilli, S. H. Pulcinelli, E. Elkaim, and V. Briois, *J. Non-Cryst. Solids* **273**, 302 (2000).
- ¹³J. Rodríguez-Carvajal, *FULLPROF*, 2001.
- ¹⁴J. Albertsson, S. C. Abrahams, and A. Kvik, *Acta Crystallogr., Sect. B: Struct. Sci.* **39**, 408 (1983).
- ¹⁵M. Winterer, *J. Appl. Phys.* **88**, 5635 (2000).
- ¹⁶S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, and M. J. Eller, *Phys. Rev. B* **52**, 2995 (1995).
- ¹⁷M. Winterer, *Nanocrystalline Ceramics* (Springer, Berlin, 2002).
- ¹⁸V. Perebeinos, S.-W. Chan, and F. Zhang, *Solid State Commun.* **123**, 295 (2002).
- ¹⁹P. Ayyub, V. R. Palkar, S. Chattopadhyay, and M. Multani, *Phys. Rev. B* **51**, 6135 (1995).
- ²⁰E. H. Kisi and M. E. Elcombe, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C45**, 1867 (1989).
- ²¹O. García-Martínez, R. M. Rojas, E. Vila, and J. J. Martín de Vidales, *Solid State Ionics* **63–65**, 442 (1993).
- ²²S. Desgreniers, *Phys. Rev. B* **58**, 14102 (1998).
- ²³C. Hormillosa and I. D. Brown, *BOND VALENCE CALCULATOR* software, McMaster University, 1993.
- ²⁴L. Galois, *Phys. Chem. Miner.* **23**, 217 (1996).
- ²⁵W. F. Pong, R. A. Mayanovic, B. A. Bunker, J. K. Furdyna, and U. Deb-ska, *Phys. Rev. B* **41**, 8440 (1990).
- ²⁶W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics* (Wiley, New York, 1975).
- ²⁷T. Agne, Z. Guan, X. M. Li, H. Wolf, T. Wichert, H. Natter, and R. Hempelmann, *Appl. Phys. Lett.* **83**, 1204 (2003).
- ²⁸A. R. West, *Basic Solid State Chemistry*, 2nd ed. (Wiley, New York, 1999).
- ²⁹M. Shim, C. Wang, D. J. Norris, and P. Guyot-Sionnest, *MRS Bull.* **26**, 1005 (2001).
- ³⁰V. Ischenko, S. Polarz, D. Grote, V. Stavarache, K. Fink, and M. Driess, *Adv. Funct. Mater.* **15**, 1945 (2005).