Formation of metallic indium-tin phase from indium-tin-oxide nanoparticles under reducing conditions and its influence on the electrical properties

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The correlation between defect structure, metal segregation, and electrical resistivity of indium-tin-oxide nanopowder upon treatment in reducing atmosphere was investigated. Morphology and defect structure have been investigated by *in situ* synchrotron x-ray diffraction and transmission electron microscopy, while traces of metallic indium have been detected by susceptibility measurements utilizing the superconducting properties of indium. With increasing treatment temperature under reforming gas the film resistivity decreases down to $\rho = 1.6 \times 10^{-2} \Omega$ cm at 330 °C annealing temperature. For even higher treatment temperatures, the resistivity increases further. This is accompanied by extractions of metallic indium. Under forming gas, grain growth could be observed at 350 °C, while in air grain growth starts at 650 °C. Furthermore forming gas causes a lattice expansion of ITO which persists in oxygen, at least for several hours. The results are discussed with respect to results published in the literature. © 2008 American Institute of Physics. [DOI: 10.1063/1.2958323]

I. INTRODUCTION

Highly tin-doped indium oxide (ITO) combines several technologically desirable properties as it is electrically conducting as well as optically transparent in the spectral range of visible light. Furthermore the plasma frequency can be adjusted via the tin-doping level, thus good reflectance in the infrared region can be achieved.¹ Even though several other transparent conducting oxides such as doped CdO, ZnO, or SnO₂ exist, In₂O₃: Sn is the most widespread representative.

With regard to the growing need for combined optoelectronic systems, there is a multitude of applications and production methods for ITO. For instance, ITO is used as transparent conducting electrode in display and solar-cell technology.² Other applications are found in electrochromic devices³ and heat-reflecting filters,¹ where the infrared absorbance is of major importance. Moreover In_2O_3 in its undoped form is described as a gas-sensing material. Doped with Pt⁴⁺ or Au³⁺ it becomes NH₃ sensitive.^{4,5}

In most applications the production of thin ITO films is necessary. For this purpose common methods of layer deposition such as evaporation of In_2O_3 and SnO_2 powders⁶⁻¹² and (magnetron) dc- and rf-sputtering^{2,13-19} spray pyrolysis^{1,5,20} are widely used.²¹

Additionally some other methods of thin-film production have evolved. The chemical sol-gel process is based on a

colloidal suspension containing metal-organic precursors of indium and tin. The polymers react forming a threedimensional network and hence creating a solid state as the solvent evaporates. This technique has been used for producing thin films of ITO (Refs. 22 and 23) and low-performance semiconductor devices.²⁴ Deposition via spin or dip coating is commonly used, but printing methods are also feasible for industrial utilization.²⁵

The idea of printing electronic films and devices has advantages because of a variable, cheap, and rapid production where no further etching steps are necessary. Stable dispersions of nanoparticles can be used as the so-called inks. Deposition on substrates by appropriate printing techniques is followed by a thermal postprocessing step. The result is a porous, nanoparticle-based thin film.

Independent of the deposition method, postdeposition treatments are applied in order to improve the properties of ITO thin films. They are usually described as annealing steps in a reducing or an oxidizing atmosphere or a sequence of For reducing atmospheres both. either forming gas^{10,19,20,22,23,26–30} or low oxygen partial pressures^{1,14,17,26,31–36} pressures $^{1,14,17,26,31-36}$ are used. Furthermore, plasma treatments $^{37-39}$ as well as wet-chemical treatments $^{40-42}$ are ways to influence ITO's surface properties. The compilation in Table I shows the change of conductivity depending on the deposition method and postdeposition treatment.

Frank and Köstlin²⁰ explained the effect of the reducing treatment through a reactivation of the dopants: Additional oxygen positioned at the unoccupied 16c site exists in the In_2O_3 lattice. Arguing with this defect they brought forward the model that the charge carrier density *n* is lowered by the formation of clusters of the additional oxygen anions and the neighboring donor cations. Additionally a distinction between reducible and nonreducible tin-oxygen associates was

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TABLE I. Compilation of literature data concerning the change of the conductivity depending on the deposition method and postdeposition treatment.

Author, year	Sample preparation	Parameters of reducing treatment	Characteristic changes of σ upon reduction
González, 2004 ^a	Bulk pellets: pressed and sintered at up to 1350 °C	pO_2 between 10^{+3} and 10^{-13} mbar	σ rises from 10 ⁺³ to 10 ⁻⁵ mbar by a factor of 3.3. From 10 ⁻⁵ to 10 ⁻¹³ mbar no pO ₂ dependence of σ
	Nanopowder pellets: pressed and sintered at 700 °C, 1 h	pO_2 between 10^{+3} and 10^{-3} mbar	σ rises from 10 ⁺³ to 10 ⁻¹ mbar by a factor of 2.6. From 10 ⁻¹ to 10 ⁻³ mbar no pO ₂ dependence of σ
González, 2001 ^{b26}	Bulk pellets: pressed and sintered at up to 1350 °C	CO/CO ₂ gas (pO ₂ 10 ⁻¹¹ mbar), 800 °C, 65 h H ₂ /N ₂ gas (4% H ₂), 500 °C, 6 h	σ rises from 601 to 1690 S cm ⁻¹ by the factor of 2.8. σ drastically increases (6 h), formation of metallic indium if exposed longer than 6 h.
Ederth, 2002 ^{c32}	220 nm thin, porous films by spin coating dispersions of nano-particles $(d \approx 14 \text{ nm})$	0.2 mbar,200/300/400 °C, 2 h	σ =0.52/0.76/2.78 S cm ⁻¹ meaning an increase by a factor of 15 / 22 / 80.
Ederth, 2003 ^{d31}	1100 nm thin, porous films by spin coating dispersions of nano-particles $(d \approx 16 \text{ nm})$	1 h in air, 1 h in N2 at either 300/400/500/650/800 °C	$\sigma = 2 \times 10^{-2}/6.3 \times 10^{-2}/1.6 \times 10^{-1}$ /3.7×10 ⁻¹ S cm ⁻¹ /1.1×10 ⁻¹ S cm ⁻¹
Ederth, 2005 ^e	600 nm thin, porous films by spin coating dispersions of nano-particles $(d \approx 16 \text{ nm})$	0.2 mbar, 500 °C, 2 h 0.2 mbar, 500 °C 2 h and 1 bar (air), 500 °C, 2 h	σ rises from 5 to 82 S cm ⁻¹ by the factor of 16. σ rises from 5 to 125 S cm ⁻¹ by the factor of 25.
Radhouane, 1998 ^f	150 nm thin films by dip coating	6.5×10 ⁻³ mbar, 450 °C, 1 h	$\sigma_{\rm max}$ =3×10 ⁺³ S cm ⁻¹ , increase by factor of 2.5.
Shigeno, 2002 ^g	200 nm thin films by dip coating 40 times	H ₂ /N ₂ gas (0.1% H ₂), 600 °C, 1 h	$\sigma_{\rm max}$ =3.2×10 ⁺³ S cm ⁻¹ , increase by factor of 6 from as deposited films.
Ishada, 1993 ^h	Crystalline/ amorphous films by e-beam evaporation	$\rm H_2$ gas flow, 400 $^{\circ}\rm C$	$\sigma = 10^{-1}$ S cm ⁻¹ , increase by factor of 6.
Han, 2006 ⁱ	50 and 90 nm thin films on polymer substrates by rf sputtering	H ₂ /N ₂ gas (5% H ₂), 150 °C, 2 h	σ =263 S cm ⁻¹ , increase by factor of 1.4 for 50 nm thickness and σ =476 S cm ⁻¹ , increase by factor of 1.5 for 90 nm thickness.
Bardos, 1989 ^j	360 nm thin films by magnetron sputtering	5×10 ⁻⁵ mbar, 393/363/314 °C, 3.3 h; followed by a subsequent annealing in oxygen gas (440 °C, 1.5 h)	σ =2.6×10 ⁺³ /2.0×10 ⁺³ /1.2×10 ⁺³ S cm ⁻¹ ; increase by a factor of 22 / 17 / 10
Gassenbauer, 2006 ^k	Thin films by magnetron sputtering at 5×10^{-3} mbar Ar/O ₂ gas with 0 to 10% O ₂ fraction		σ varies from $1.8 \times 10^{+1}$ to $4.6 \times 10^{+3}$ S cm ⁻¹ , factor of 256.
Lan, 1997 ¹	Thin films by sputtering; annealing either in vacuum at 200 °C or in air at 230 °C	Atomic hydrogen generated by PECVD, 15 min	σ rises by a factor of 3 (vacuum annealed) / 2.5 (air annealed). 100 nm metallic indium balls form on the surface.

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TABLE I. (Continued.)

Author, year	Sample preparation	Parameters of reducing treatment	Characteristic changes of σ upon reduction
Frank, 1981 ^m	Thin films by spray pyrolysis	PO_2 between 10^{+3} and 10^{-27} mbar	σ rises from 10 ⁺³ down to 10 ⁻²⁴ mbar by the factor of 24. Below 10 ⁻²³ mbar irreversible decomposition
Major, 1986 ⁿ	500 nm thin films by spray pyrolysis	Hydrogen plasma at a substrate temperature of 250 °C, 0.5 h	σ rises by a factor of 1.5. Reduction to metallic indium at the surface.
Reference 34. Reference 26. Reference 32.			

^dReference 31. ^eReference 33. ^fReference 35. ^gReference 27. ^hReference 10. ⁱReference 19.

^jReference 14.

^kReference 17.

^lReference 49.

^mReference 1.

ⁿReference 39.

made. Defect oxygen, which is bound in a reducible state, can be removed from the lattice by a reducing postdeposition treatment. Consequently fewer donor electrons are being passivated and, thus, the specific conductivity σ increases. This model could be experimentally and theoretically substantiated and enhanced by González *et al.*,³⁴ Warschkow *et al.*,^{43,44} and other groups. The existence of tin-oxygen clusters was experimentally verified by Mössbauer spectrometry.⁴⁵

Application-oriented works repeatedly reported the occurrence of metallic indium in different ITO layers.^{4,10,46–48} This formation is usually driven by strongly reducing conditions such as plasma-enhanced chemical-vapor deposition (PECVD),^{39,49} ultrahigh vacuum (UHV),^{5,12} and hydrogen gas³⁸ or acids in wet chemistry.^{40,41} But also the neutrondiffraction study of González *et al.* mentioned the occurrence of metallic indium after a reduction with the forming gas.²⁶ Apparently the reported reducing treatments cannot only remove tin-oxygen associates but they can also cause the formation of metallic indium at the surface of defect-containing indium oxide.

Despite this fact, hardly any attempts have been made to investigate the relation between the metallic-indium phase and the changes in conductivity. Therefore the main objectives of this work are (i) to investigate structural differences between ITO in oxidizing and in reducing atmosphere, (ii) to detect traces of metallic indium in samples that have undergone an annealing in reducing conditions, and (iii) to correlate the findings of the structural changes to the specific resistivity of accordingly reduced ITO thin films.

X-ray powder diffraction (XRPD) with synchrotron radiation was performed in defined atmospheric conditions. This was done for the purpose of *in situ* measuring the occupation of the 16c position and the resulting changes in the lattice parameter *a*. Other samples were reduced in forming gas and magnetic low-temperature susceptibility measurements with a superconducting quantum interference device (SQUID) were used as the detection method for traces of metallic indium and tin. This method makes use of the superconductivity of the metals below 3.4 K. The strong diamagnetic influence of the superconducting phase on the susceptibility sensitively distinguishes metallic indium from indium atoms which are bound in the indium-oxide lattice. Moreover a transmission electron microscope (TEM) investigation was performed to gain insights into the morphological appearance of the metallic phase. The powders from SQUID and TEM were also used for complementary XRPD measurements with copper radiation. This helped quantifying the amounts of metallic indium and monitoring the grain growth. The correlation of these experiments to the resistivity and transparency of the ITO was done using spin-coated films of the same starting material which was reduced accordingly.

II. EXPERIMENTAL

A. Sample material

1. Powder samples

As sample material ITO nanoparticles were used because of the huge surface-to-volume ratio. The particles were produced and provided by Evonik Degussa. According to the product information sheet the tin content was approximately 5 at. %. At room temperature (RT) the average particle diameter was ascertained to 9.1 nm from XRPD diffractograms using the Scherrer formula. TEM images (Fig. 1) confirm this value with the exception of some considerably larger particles. Figure 1 also shows the monocrystalline nature of the nanoparticles which justifies the use of the Scherrer formula.



FIG. 1. TEM images of the used ITO nanoparticles collected on a standard copper TEM grid. The overview image (a) gives an impression of the size distribution and nonspherical shape of the particles. The mean diameter of the particles is approximately 10 nm (9.1 nm from XRDP). The high-resolution image (b) demonstrates very good crystallinity.

For SQUID, XRPD, and TEM investigations, ITOpowder samples were reduced in a tube furnace at temperatures between 350 and 450 °C with a mixture of 8 vol % H_2 and 92 vol % N_2 gas at a flow rate of 1.00 l/min for 2 h. A heating ramp of 10 °C/min in the beginning and cooling at ambient temperature within the forming gas flow completed the process. All powders were transferred to a glovebox inside the tube, so that degradation under ambient conditions was avoided.

2. Thin films

Thin films of ITO nanoparticles were produced in the following way: Standard glass substrates were cleaned in an ultrasonic bath, each 15 min in acetone, ethanol, and isopropanol. Substrates were dried with nitrogen gas. For the subsequent spin coating, alcohol-based ITO dispersions were used. 200 μ l of the dispersion were placed on the glass substrate, the spin-coating program was started immediately afterwards (180 s at 2000 rpm; acceleration: 4000 rpm/s).

The as-obtained thin films were temperature treated in a muffle furnace at 450 °C for 90 min in air. The applied heating rate was 10 °C/min. After the annealing, samples were slowly cooled down in the muffle furnace over night. The second temperature treatment was performed in a tube furnace. A constant gas flow of 1.00 l min⁻¹ of a forming gas (8% H₂+92% N₂) was applied. The heating ramp was again 10 °C/min. The duration of the second temperature treatment was 120 min. Samples were rapidly cooled down by pulling the tube out of the furnace, while still maintaining the gas atmosphere inside the tube. The annealing temperature was varied between 300 and 450 °C. The thin films were immediately transferred into a glovebox for characterization in order to avoid degeneration effects which might occur under ambient atmosphere.

B. Characterization

1. Synchrotron XRPD

Synchrotron XRPD measurements were conducted at the beamline B2 of the electron-storage ring DORIS III which is part of the HASYLAB, Hamburg.⁵⁰ The specific setup allowed controlling of the temperature and gas atmosphere during the experiments. Temperatures up to 800 °C and allowed control setup.

ternately 99.9% pure oxygen, argon, or hydrogen gas could be applied. The above described untreated ITO nanopowder was filled into 1 mm quartz capillaries and attached to the gas supply.

At a wavelength of 0.47 Å two different measurement cycles were performed. Firstly, gas atmosphere was kept constant at 30 ml min⁻¹ and 0.7–1 bar hydrogen, whereas temperature was raised stepwise from RT to 450 °C. Secondly, temperature was kept constant at 400 °C while the atmosphere was switched in the order $Ar \rightarrow O_2 \rightarrow Ar \rightarrow H_2$ $\rightarrow Ar \rightarrow O_2$. Three measurement cycles of 20 min were run after each change of temperature or atmosphere, respectively. The diffractograms were evaluated using the Rietveld refinement method⁵¹ in terms of changes in lattice constant, occupation of the 16*c* site, and appearance of additional phases.

2. XRPD

For the following series of experiments, ITO-powder samples were reduced in a tube furnace at 350, 360, 370, 375, 400, and 450 °C under the above described conditions. Capillaries of 0.3 mm diameter were filled with the reduced powder and diffractograms were recorded with a STOE STADI P diffractometer in Debye–Scherrer geometry. A Rietveld refinement was conducted in order to detect and quantify a potential indium phase in the reduced powders as well as the average isotropic particle diameter with the help of the Scherrer formula implemented in the Rietveld software FULLPROF.⁵¹

3. Measurement of the susceptibility

The magnetic susceptibility χ_m was measured with a Quantum Design SQUID MPMS XL at temperatures between 80 and 2 K. Because of the high sensitivity of a SQUID, this method was able to detect traces of superconductive, metallic indium where regular XRPD and other methods failed.

The same reduced powders as for the XRPD measurements were used. Another powder sample was reduced under pure hydrogen gas at a pressure of 100 bars for 2 h. Samples were poured into capsules in the inert atmosphere of a glovebox. During the sample transfer from the glovebox to the SQUID, the prepared samples were exposed to air for approximately 1 min. Susceptibility of one untreated ITO sample was also measured.

4. TEM

For the complementary TEM study ITO nanopowder which was reduced to 450 °C under the above described conditions was used. The powder sample was dispersed in ethanol under inert conditions and dropped onto a standard carbon-coated Cu grid. The samples were loaded into a Gatan vacuum-transfer holder within a glovebox and transferred to the microscope without exposure to ambient atmosphere. The investigations were performed with a FEI Tecnai F20 ST. To identify indium-rich regions, we used scanning transmission electron microscopy (STEM) combined with energy dispersive x-ray spectroscopy mappings of the oxygen *K*-edge and the indium *K*-edge.



FIG. 2. X-ray diffractograms of ITO nanopowders measured at the HASYLAB, Hamburg, with synchrotron radiation (λ =0.047 nm). (a) Reference measurement in Ar atmosphere and Rietveld refinement of the data. The difference plot between measured and calculated data and the Bragg positions is shown as well. (b) Series of measurements in hydrogen atmosphere. The temperature is raised stepwise from RT to 450 °C. Due to the formation of metallic indium (liquid), the background intensity increases and the reflex intensity decreases constantly.

5. Resistivity and optical transmission

The electrical resistance *R* of ITO thin films was measured in four-point-probe setup inside the glovebox. The specific resistivity ρ was calculated according to

$$\rho = R \frac{2\pi}{\ln(4L)} d,\tag{1}$$

L is a correction factor and *d* the thickness of the thin film. For the given geometry, we used L=1.8336 calculated according to Ref. 52. The thickness of the samples was measured using a Dektak profilometer type 6 M (Veeco). The optical transmission of the thin films was measured at a homemade setup.

III. RESULTS

A. Structural changes of ITO in different gas atmospheres

In order to find structural changes of the ITO samples occurring during treatment in different gas atmospheres, *in situ* synchrotron measurements were used. In the first cycle the hydrogen gas flow was kept constant and the temperature was increased step by step. As a reference, the refinement of the structural parameters based on a measurement of untreated ITO nanopowder in argon at RT can be seen in Fig. 2(a). Due to reflex broadening in the nanoparticular samples and short measurement times, the occupation of the 16*c* site could not reliably be determined. At the beginning of the series, the lattice constant was 1.0079 ± 0.0001 nm in argon gas [Fig. 2(a)].

With increasing temperature in hydrogen atmosphere, a loss of reflex intensity in combination with a growth of the amorphous background was seen, beginning between 250 and 300 °C [Fig. 2(b)]. At 450 °C, the color of the sample had turned to a metallic gray. Diffractograms below the melting point of metallic indium (T_m =156.61 °C) revealed an

increasing amount of metallic indium (space group: I4/mmm) in the sample. Additionally, the lattice constant increased linearly with temperature. At 450 °C, the refined lattice constant measured *in situ* within pure hydrogen was 1.0112 ± 0.0001 nm.

In the second series, the temperature was kept constant at 400 °C and the gaseous atmosphere was varied in the order $Ar \rightarrow O_2 \rightarrow Ar \rightarrow H_2 \rightarrow Ar \rightarrow O_2$. Even though, the *in situ* measurements were set up to provide a maximum comparability, the changes in the refined oxygen occupancy of the 16*c* site between the varying atmospheres at 400 °C were within the experimental error under argon and oxygen atmosphere (steps 1–3), but the color of the ITO nanopowder switched from blue to a yellowish white in oxygen. In hydrogen atmosphere (step 4) the lattice constant a steadily increased from 1.0077 to 1.0085 nm. This expansion was not reversible under a subsequent treatment with an oxygen atmosphere. The evolution of the lattice parameter during this series can be seen in Table II.

B. Detection of traces of metallic indium

It was found that the reducing conditions used for the *in situ* synchrotron measurements were strong enough for the reaction

TABLE II. Evolution of the lattice parameter a (nm) with the applied gaseous atmosphere. ITO powder samples were exposed to varying gaseous atmosphere $(Ar \rightarrow O_2 \rightarrow Ar \rightarrow H_2 \rightarrow Ar \rightarrow O_2)$ while the temperature was kept constant at 400 °C. The lattice parameter was obtained from Rietveld refinement of the *in situ* synchrotron x-ray diffraction pattern.

Atmosphere	Lattice parameter a (nm)	$\Delta a \ (\mathrm{nm})$
Ar	1.0079	
O ₂	1.0077	-0.0002
Ar	1.0077	
H ₂	1.0085	+0.0008
Ar	1.0083	-0.0002
O ₂	1.0083	



FIG. 3. Magnetic susceptibility measurements of samples annealed at different temperatures in reducing atmosphere (forming gas with 8% hydrogen, 1.00 l/min, 2 h). Susceptibilities χ are normalized to the 7 K values. A sudden decrease in susceptibility around 3.4 K is a proof for metallic, superconductive indium (T_c =3.4 K) in the samples. Therefore indium occurs at annealing temperatures of 370 °C and higher. In pure hydrogen gas, the ITO nanoparticles are almost entirely reduced to indium.

$$(\text{In}_{1-x}\text{Sn}_x)_2\text{O}_3 + 3\text{H}_2 \xrightarrow{250 \text{ °C}} 2 \text{ In}_{1-x}\text{Sn}_x + 3\text{H}_2\text{O}.$$
 (2)

Since reducing treatments in hydrogen gas are often used for an annealing of ITO thin films, the detection of small traces of metallic indium after such treatments is the intention of the following series of experiments. For that purpose ITOpowder samples were reduced in a tube furnace at a constant gas flow of 1.00 l/min in 8% H₂ containing forming gas at different temperatures between 350 and 450 °C. In order to detect small amounts of metallic indium and tin, it was taken advantage of their superconducting properties below their critical temperatures T_c of 3.4 and 3.7 K, respectively. Below this temperature they show ideal diamagnetic behavior which can be clearly visualized as a negative influence on the susceptibility of the sample. Therefore, the as-obtained samples were characterized by magnetic low-temperature susceptibility measurements with a SQUID. Using this method, metallic indium can be distinguished sensitively from indium tin oxide. For completeness, XRPD and TEM of the powder samples were performed.

The measurement of the susceptibility of the reduced ITO nanopowders is shown in Fig. 3 for the temperature range between 5 and 2 K. For a better comparability, the measurements are normalized. Starting for annealing temperatures between 360 and 370 °C, the transition of indium (tin) to its superconductive phase is observed in the SQUID measurements, the signal becomes stronger with increasing annealing temperature. Annealing at 400 and 450 °C in the 8% H₂ gas flow produced a powder with a very intense diamagnetic signal of the superconducting metals.

All powders were complementarily characterized by XRPD. Increasing amounts of metallic indium could be extracted from the Rietveld analysis for samples annealed at 400 and 450 $^{\circ}$ C (shown in Fig. 4). Here, the indium fraction was calculated to 13 wt % for the 400 $^{\circ}$ C annealed sample



FIG. 4. Rietveld Refinement of x-ray diffraction data collected on the ITO nanopowder which was annealed at 450 °C under reducing conditions (1.00 l/min, 8 vol % hydrogen). The inset shows the two strongest indium reflexes (*I4/mmm*). The calculated indium fraction was 24 wt %. A mean isotropic grain size of 23.7 nm was determined for the ITO phase.

and to 24 wt % for the 450 °C annealed sample. Below 400 °C annealing temperature, indium proportions were too small to be detectable by XRPD.

Additionally, the mean particle size of the ITO particles was calculated from the peak shape. It was found that the diameter increased upon annealing in hydrogen atmosphere from 9.1 nm for the RT sample to 23.7 nm for the 450 °C annealed sample. This distinguishes the annealing in a forming gas stream from an annealing in air. Up to 550 °C, no changes of the mean particle diameter (d=9.1 nm) were observed in oxygen containing atmosphere. Above 650 °C, the temperature-induced sintering of the ITO nanoparticles started. In contrast to this, a significant growth is already observable at 350 °C in hydrogen containing atmosphere (compare compilation of Fig. 7).

A complementary TEM study was carried out on the sample which was reduced at 450 °C. Figure 5 (images B–D) shows that indium spheres with a size between 100 and 800 nm form. ITO nanoparticles are attached to these spheres. Elemental maps, as shown in Fig. 6, prove that the observed spheres are mainly composed of indium. It has to be noted that the attempts to reduce ITO films of a few nanometers' thickness directly on copper grids and graphite-coated copper grids did not lead to the formation of an In–Sn phase in the layers [compare Fig. 5(a)]. Apparently, more than a few monolayers are necessary to observe the formation of indium spheres.

For all the methods used in this study, the fraction of tin was too small to be distinguishable from the main indium fraction. Therefore no statement can be made about the precise In–Sn phase composition.

Further experiments have given an indication that apart from the annealing temperature, the hydrogen concentration and the gas flow also strongly influence the formation of the metallic indium, yet the experiments are not shown in this contribution.



FIG. 5. (Color onlie) TEM images of self-supporting layers of ITO nanopowder. (a) Reference image of ITO nanopowder as it was regularly found for untreated samples (without any metallic indium). (b) Sample annealed at 450 $^{\circ}$ C and 1.00 l/min of 8 vol % hydrogen. (c) and (d) show the same position as (b) but with higher magnifications—the shown detail is indicated by a square. Indium balls of the size of approximately 100 nm, exemplarily indicated by an arrow, are found in which the ITO nanopowder is still encased.

C. Influence of the reduction in hydrogen on resistance and optical transmission of spin-coated thin films

To study the influence of the metallic indium-tin phase found under reducing conditions (8% H₂, 1.00 l/min gas flow) on the resistivity and optical transmission, thin films of the same starting material were produced by spin coating alcohol-based ITO dispersion onto glass substrates. In the first step, the thin films were temperature treated 1 h at 450 °C in air in order to burn out the organic solvent. In the second step, the thin films were reduced in the same tube furnace as used for the other studies at 1.00 l/min and 8% H₂ in the forming gas at temperatures between 300 and 450 °C. Figure 7 shows the specific resistivity and optical transmission of the spin-coated thin films. For comparison, the relative change of susceptibility (SQUID) at the transition tem-



FIG. 6. (Color online) ITO nanopowder annealed at 450 °C under reducing conditions (1.00 l/min, 8 vol % hydrogen). Left: TEM dark field image of indium drops within the ITO layer. Right: STEM image of the marked area together with the corresponding elemental mappings of the oxygen *K*-edge and indium *K*-edge. The investigated droplet is clearly enriched in indium and depleted of oxygen.



FIG. 7. Compilation of the changes in ITO samples at different annealing temperatures in forming gas with 8% hydrogen. (a) Optical transmission and (b) specific resistivity of spin-coated ITO thin films. (c) Relative change of susceptibility (SQUID) at the transition temperature of indium (T_c = 3.4 K), expressed as the fraction $\chi(2.4 \text{ K})/\chi(4.0 \text{ K})$, measured using powder samples. (d) Change of the mean particle diameter obtained from XRPD of powder samples. The lowest value for the resistivity is obtained by annealing at 340 °C which is 30 °C below the temperature where the detection of metallic indium was first possible (370 °C).

perature of indium (T_c =3.4 K) and change of the mean particle diameter (XRPD) obtained from the nanocrystalline ITO are included within this figure.

The optical transmission decreases drastically at annealing temperatures higher than 390 °C. At 370 °C, where already a very clear indication for metallic indium was found by SQUID, the optical transmission was still around 97%.

The specific resistivity ρ shows a minimum in its progression. The lowest value for the resistivity was measured at 340 °C with $\rho = 1.16 \times 10^{-2} \Omega$ cm. Compared to the resistivity of the sample which was only treated at 450 °C in air, an

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improvement by a factor of 30 was achieved. Higher annealing temperatures lead to an increase in ρ .

IV. DISCUSSION

The *in situ* synchrotron XRPD measurements performed at constant temperature of 400 °C with subsequent argon, oxygen, and argon atmosphere did not show any changes in the structural properties of ITO, neither in the lattice constant nor in the occupancy of the 16c site. However, an increase in the lattice parameter was observed, after the material was exposed to hydrogen, which implies the occurrence of structural changes. The expansion of the lattice constant a remains after the H₂- treatment. The explanation of Frank and Köstlins²⁰ for this is the removal of oxygen defects from the regularly unoccupied 16c site in ITO's bixbyite structure. According to their work, oxygen anions compensate the effective charge of the tin cations. With less defect-oxygen anions left after a reduction, the repulsion forces between the tin cations cause an increase in lattice parameter. This model is in accordance with works from the group of Gonzales et al.³⁴ who carried out highly precise ex situ synchrotron XRD, time-of-flight-neutron diffraction, and extended x-ray absorption fine structure experiments on ITO nanopowders with 3-4 at. % tin. They correlated their finding with the measured occupation of the 16c site and the formation of reducible and nonreducible tin-oxygen associates. The results are also supported by the calculations of Warschkow,⁵³ validating the theory of Frank and Köstlin.

Moreover the synchrotron-XRPD results showed that in oxygen-rich atmosphere up to 400 °C no structural changes occur whatsoever. This holds both for before as well as after treatment with reducing H₂ gas. Hence, the removal of interstitial oxygen seems to be an irreversible process within the time of measurement. Furthermore, diffusion of oxygen into the lattice seems to be strongly hindered. This result is unexpected because it is hard to accept that oxygen can be easily removed from a lattice with smaller lattice constant, while a back diffusion of oxygen into a lattice with large lattice constant is hindered. The explanation could be that the oxygen was offered within a bound molecular state of O₂ during the oxidizing treatment, whereas oxygen atoms were removed out of the crystal during the reducing treatment. In that case, the breaking of the oxygen-oxygen binding would be the limiting factor.

Gassenbauer¹⁷ investigated sputtered ITO thin films with surface-sensitive spectroscopy methods (x-ray photoelectron spectroscopy, ultraviolet photoemission epectroscopy) and brought forward the model of a thin surface layer with a reduced level of free charge carriers. According to the oxygen-defect model, this would correspond to increased oxygen content in the surface region. Harvey⁵⁴ argued that this layer could form during the cooling procedure of the sample preparation. Considering the results of the present work, the threshold temperature for diffusion of oxygen into the ITO lattice has to be at least higher than 400 °C. Otherwise changes in the structure should have been seen in the presented measurements as it was possible for the hydrogen treatment. The synchrotron XRPD (Fig. 2), SQUID (Fig. 3), XRPD (Fig. 4), and TEM (Figs. 5 and 6) studies all prove the formation of a metallic In–Sn phase from ITO when the samples are heated in 100% or 8% hydrogen gas, respectively. In pure hydrogen and a gas flow of 30 ml/min, the formation of the metallic phase started between 250 and 300 °C [Fig. 2(b)]. The liquid-indium phase ($T_m \approx 156$ °C) (Ref. 55) caused a proportional decrease in intensity of the ITO reflections combined with increasing background intensity.

With the highly sensitive susceptibility measurements, traces of metallic In (Sn) were detected starting at 360 to 370 °C in 8% hydrogen gas and a flow rate of 1.00 l/min. Similar conditions are commonly used in industrial processes and in literature. The standard analysis with XRPD, however, was not sensitive enough to detect the indium phase up to an annealing temperature of 400 °C. This could be a reason why this phenomenon is so rarely discussed in literature. As seen in Fig. 3 the onset of superconductivity deviates from the critical temperature of indium $(T_c=3.4 \text{ K})$ for samples with higher annealing temperatures and higher In (Sn) amounts accordingly. This effect can be interpreted in terms of a changing material's composition and particle size as well as by impurity effects within the In-Sn balls. These factors strongly influence the superconducting properties.^{56,57} The vast size distribution of the occurring In (Sn) particles is probably responsible for the soft onset of superconductivity.

TEM investigations of ITO samples reduced at 450 $^{\circ}$ C in forming gas gave insights into the morphological appearance of metallic indium, if the amount is sufficient. It occurs in the form of several hundred nanometer large spherical particles with attached ITO nanoparticles. The In (Sn) is in a liquid state at the temperature of formation. Hence, the reduction of surface tensions should be the driving force for the agglomeration to larger In (Sn) droplets. A similar morphology was observed on the surface of sputtered ITO films by Lan and Kanicki.⁴⁹ They had treated their samples either by hot-wire chemical-vapor deposition or PECVD.

The refinement of the structural model based on complementary XRPD measurements of the annealed ITO nanopowder showed that the mean grain size increased upon annealing in 8% hydrogen already at a temperature of 350 °C. An ITO sintering study of Kim et al.⁵⁸ as well as own sintering experiments of ITO nanoparticles annealed in air showed that no particle growth was found at temperatures below 650 °C. Sintering and grain growth are driven by diffusion and therefore favor a high vacancy concentration. As discussed above, the reducing atmosphere removes oxygen anions from the lattice at elevated temperatures, thus giving rise to an enhanced activity of diffusion-especially at the surface of the nanoparticles. Therefore sintering going along with a grain growth can occur at lower temperatures in reducing atmosphere than in oxygen-rich atmosphere. This model is also supported by the findings of a synchrotron photoemission study of Brinzari et al.⁵ Their results suggest a strong reduction of the topmost ITO layer to an almost oxygen-free indium plane under UHV conditions. The applied temperature treatments took place at \geq 300 °C.

The influence of the discussed structural and morpho-

logical changes on the electrical and optical properties of nanoparticular ITO films is of major importance for technical applications. The best value for the specific resistivity of the spin-coated ITO thin films was found for an annealing at 340 °C with ρ =1.16×10⁻² Ω cm. The lowest temperature at which traces of metallic indium could be detected without a doubt was 370 °C. At this temperature, the optical transmission of the ITO layers was still at its maximum. None-theless, traces of the metal already have a negative influence on the conductivity (Fig. 7).

The work function of bulk indium is 4.12 eV,⁵⁹ this of bulk ITO is about 4.8 eV. Thus, the metal and the semiconductor are supposed to build an Ohmic contact according to the Schottky model. Following this model, carriers would inject from the metal into the ITO and form an accumulation region at the interface of the ITO. The conductivity should increase because of an increased carrier concentration. None-theless, a negative influence of the metallic indium on the conductivity was observed. The Schottky model is based on a planar interface between a metallic and a semiconducting layer. The present work deals with a morphology of loosely packed nanoparticulate films with metallic inclusions. Therefore, the Schottky model might not be applied without restrictions.

TEM observations showed the tendency of the metallic indium to form metal aggregates. The XRPD analysis ascertained the sintering of the ITO nanoparticles. Both result in morphological changes of the thin film. We expect that the disturbance of the films' morphology, e.g., the formation of microcracks, is the main influence on the resistivity.

To compare the present results to literature data, it has to be stated that not only the annealing temperature but also gas flow (which includes the furnace geometry) and hydrogen concentration play a role. González et al.²⁶ (Table I) have annealed pressed and sintered ITO pellets at 500 °C in a 4% hydrogen/nitrogen mixture. They observed that this treatment increased the conductivity σ strongly. When the samples were exposed to the reducing conditions for a longer time, metallic indium was found. Thus, the reported increase in σ lies in a window of time, temperature, and hydrogen concentration which is close to the region where metallic indium forms. Slightly longer exposure times (or in our study exposure temperatures) would shift the reaction of Eq. (2) toward the formation of indium. On the other hand, temperatures lower than 340 °C lead to higher values of the resistivity indicating a less ideal defect structure of the material. The temperature window for optimizing the specific resistivity is therefore relatively small (Fig. 7).

Samples which come close to the investigated type of the present study are found at Ederth *et al.*^{31,33} (Table I). Here, 600 nm thick spin-coated thin films of ITO nanoparticles (average diameter: 16 nm) were temperature treated in a technical vacuum of 0.2 mbar at 500 °C. This treatment improved the initial value for the specific resistivity by a factor of 22 which is in the region of the results of this work. While the main intertransport mechanism was found to be dominated by tunneling of charge carriers between clusters of ITO nanoparticles, the changes in the samples during vacuum annealing could not be explained entirely. Applying the findings of the present work, it is most likely that a higher surface activity of the ITO nanoparticles in the vacuum atmosphere leads to improved electrical contacts between the particles. At the same time an oxygen-depleted particle surface should form. The main difference between the experiments of Ederth *et al.*^{31,33} and this work is the reducing conditions since Ederth *et al.* used a low oxygen partial pressure instead of a reducing forming gas. The detailed differences between these two methods are not yet clear. But since indium was already detected at 300 °C under UHV (2×10^{-10} mbar) by Brinzari *et al.* it is likely that the formation of metallic indium is found accordingly under vacuum annealing conditions.

V. CONCLUSION

The electric film resistivity of nanoparticulate ITO layers undergoes a minimum for a thermal post-treatment under forming gas. The resistivity decreases with increasing posttreatment temperature up to 340 °C, most probably due to a change in the oxygen-defect concentration. At temperatures higher than 350 °C, metallic indium or indium/tin is extracted, which correlates with an increase in resistivity and a decrease in transparency. The decrease in resistivity is explained by morphological changes in the nanoparticulate layer due to the tendency of metallic indium to form larger aggregates and microcrack formation during sintering. The lowest film resistivity was observed around 340 °C, however, the appearance of metallic phases depends strongly on film morphology, gas flow, and hydrogen content. While under hydrogen atmosphere grain growth starts already around 350 °C, there is no grain growth in oxygen atmosphere up to 650 °C. The enhanced grain growth in hydrogen atmosphere is explained by an enhanced surface diffusion under reducing conditions. The lattice constant of ITO increases under hydrogen atmosphere. But a subsequent oxygen treatment does not reverse the lattice widening at least for the measure time of several hours. The difference is maybe due to the fact that atomic oxygen diffused out of the In₂O₃ lattice, whereas it was offered in a bound molecular state of O2 for the indiffusion. In that case, the breaking of the O₂ molecule would be the limiting factor.

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