**ABSTRACT**

ZnO doped with Fe$_2$O$_3$ or In$_2$O$_3$ show characteristic inversion domain structures comprising two types of inversion domain boundaries (IDBs): basal IDBs parallel to (0001) planes, and pyramidal IDBs parallel to (2 1 1 5) planes. Energy-filtered transmission electron microscopy imaging showed that dopants are essentially located in the IDBs. Quantitative electron energy-loss spectroscopy analysis revealed that unaffected ZnO domains contain up to 0.4 at.% Fe in solid solution, whereas inverted domains are Fe depleted. Variable-beam EELS analysis indicated an Fe content equivalent to one monolayer in basal IDBs. The number of IDBs within a defined volume directly correlates with the dopant concentration measured by energy-dispersive spectroscopy analysis in spectroscopic STEM imaging (SIX).

**KEYWORDS**

transmission electron microscopy, electron energy-loss spectroscopy, energy-dispersive X-ray spectroscopy, zinc oxide, dopants

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**INTRODUCTION**

Zinc oxide (ZnO) is a highly versatile material used in a multitude of technological applications. Its unique combinations of optical, electronic and piezoelectric properties can be controlled by doping with other metals such as iron, manganese, cobalt or indium.

ZnO materials doped with ambivalent 3d transition metals are considered as promising candidates for spintronic applications because of novel combinations of ferromagnetism and semiconductive properties. Undoped ZnO crystallizes into the non-centrosymmetric wurtzite structure with alternating (0002) layers of tetrahedrally co-ordinated O$^-$ and Zn$^{2+}$ ions stacked along the c axis. For reasons of charge balance, trivalent Fe$^{3+}$ or In$^{3+}$ cannot be substituted on regular cation sites, thus resulting in a characteristic inversion domain structure with two types of planar inversion domain boundaries (IDBs): basal IDBs parallel to (0001) lattice planes, and pyramidal IDBs parallel to (2 1 1 5) planes, respectively.

The number of IDBs is directly correlated to the dopant concentration; quasi-periodic structures are observed at dopant concentrations $\geq$ 0.5 at.% of cations (Figure 1). In the present investigation the distribution of trivalent Fe and In dopants in ZnO was studied by a combined quantitative electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS) analysis.

**MATERIALS AND METHODS**

Materials

The starting materials were high-purity powders of zinc oxide (ZnO), hematite ($\alpha$-Fe$_2$O$_3$) and indium oxide (In$_2$O$_3$) (all 99.999% purity, from Sigma-Aldrich). Sintered material was prepared by dry pressing of appropriate powder mixtures followed by sintering at 1350°C for 24 h.

In-doped ZnO nanorods were grown by the vapour-liquid-solid (VLS) process using Au catalyst particles on fused silica substrate.

**Specimen preparation**

TEM specimens were prepared from sintered materials by standard procedures, i.e. mechanical grinding, dimpling and ion beam thinning. ZnO nanorods were deposited on holey carbon film.

**Electron Microscopy**

EDS and EELS measurements were performed at 300 kV in a Philips (FEI) CM 300 ST analytical TEM/STEM equipped with a Noran EDS System SIX (Thermo Fisher) and a Gatan 666 PEELS spectrometer.

High-resolution and energy-filtered (EFTEM) imaging were performed in a Philips (FEI) CM 300 UT FEG TEM/STEM with a Gatan Imaging Filter (GIF).

High energy-resolution EELS measurements were performed in a Cs-corrected and monochromated Zeiss Libra 200FE CRISP Special TEM/STEM system equipped with an Omega-type in-column energy filter with an attainable energy-resolution of $\approx$ 0.15 eV.

A relatively large probe size (5 nm) was used in STEM for spectroscopic imaging by X-ray (SAX) in order to increase counting statistics and signal to noise ratio at the expense of image resolution.

**Figure 1:** Brightfield transmission electron microscope image of periodic inversion domain structure observed in Fe$_2$O$_3$/ZnO$_{0.95}$, Z. A. (0 1 1 0). Inversion domain boundaries (IDBs) are parallel to (0001) basal plane (some are marked by blue arrows) and pairs of (2 1 1 5) pyramidal planes (indicated by red arrows).
RESULTS
Elemental mapping in energy-filtering TEM indicated that dopants were essentially located within the IDBs (Figure 2), however, it did not allow for a quantitative assessment of dopant concentrations [1].

Individual ZnO domains and IDBs as observed in the domain structure (Figure 3) were analyzed by EELS spot measurements with high spatial resolution in diffraction/nanoprobe mode (regions are indicated by open circles). EEL spectra as acquired (Figure 4) did not allow a direct quantification of dopant concentrations.

Measurements on pure ZnO standards (Figure 5) indicated that corrections for O-K EXELFS oscillations were necessary (Figure 6) for an accurate quantitative analysis of Fe or Mn at low concentrations in ZnO [2]. Corrected quantitative measurements yielded a solid-solubility <0.4 at.% Fe in unaffected ZnO domains (ZS), whereas in the inverted domains (Z0) Fe was depleted (<0.1 at.% Fe).

Since the probe size (3 nm) exceeded the lateral width of IDBs in edge-on orientation, contributions from adjacent matrix regions had to be taken into account in quantitative measurements. Thus, the Fe content in single basal IDBs was measured by EELS using the variable beam-diameter method [1], yielding an effec-

Analysis
For a quantitative assessment of Fe dopants at low concentrations in ZnO domains, the Fe-L signal in EELS was corrected for O-K EXELFS oscillations [2]. A normalized correction function was obtained from the background-subtracted EELS signal measured from pure ZnO reference material.

The method of variable beam-diameter analysis was used to assess the Fe dopant concentration in basal IDBs. This method, initially developed for EDS analysis of planar interphase interfaces [7, 8], was adapted to EELS analysis using probe diameters between 1.6 and 5 nm in diffraction nanoprobe mode.
EELS/EDS of Dopants

**Figure 5:**
EEL spectra from pure ZnO reference material. Background-subtracted signal reveals O-K EXELFS oscillations in the energy regions $\Delta E \approx 640$ eV (vicinity of Mn-L edge) and $\Delta E \approx 710$ eV (vicinity of Fe-L edge). Difference spectrum used for EXELFS correction (two-window background model A-fit [5]).

**Figure 6:**
Extraction of net Fe-L signal (5) by subtracting correction function (4) from background-subtracted EELS signal (3). Correction function obtained by smoothing and normalizing the difference spectrum in Figure 5.

**Figure 7:**
Quantitative EELS analysis of dopant concentration in basal IDB by means of the variable beam method.

(a) Schematic of illumination geometry with electron probe of radius $R$ centred on basal IDB in edge-on orientation. The ratio of the effective areas is a linear function of $R$.

(b) Ratio of apparent concentrations $C_{Zn}/C_{Fe}$ from a series of EEL spectra acquired with variable electron beam radii. The measured slope of 5.8 nm$^{-1}$ yields an effective width $d \approx 0.27$ nm for basal IDB corresponding to one monolayer of Fe.

**Figure 8:**
Inversion domain structure in Fe$_2$O$_3$ (ZnO)$_{15}$.

(a) Periodically spaced basal IDBs are observed in edge-on orientation. TEM-BF image, Z. A. [1 1 2 0]. Boxed area indicates sample region analyzed by EDS-SIX in STEM (256 x 196 pixels).

(b) HR-EEL spectrum recorded at 0.15 eV resolution showing the Fe-L$_{2,3}$ ionization edge (background subtracted). Subtracting the continuum background modeled by Hartree-Slater type function (green) yields net intensities of white lines (1.5 eV integration windows centred at peak maxima indicated in shaded blue). Valence-sensitive white-line intensity ratio Fe-L$_3$/Fe-L$_2$ » 7.2 indicates trivalent oxidation state Fe$^{3+}$.

The results from EELS analyses were verified by EDS measurements in STEM spectroscopic imaging by X-rays (SIX). Well-defined sample areas containing IDBs in edge-on orientation were scanned (256 x 196 pixels) as indicated in Figures 8 and 9 and quantitatively analyzed by SIX.

The number of IDBs within the scanned region (scan lines oriented parallel to c axis) yielded a quantitative correlation between the ratio of (0002) cation layers in IDBs (number of Fe or In layers) and Zn layers within the ZnO domains in-between (dopant:Zn layer ratio), and corresponding dopant concentration within the scanned region as measured by EDS (Table 1).

EDS-SIX measurements in sintered Fe-ZnO and In-ZnO, where thermal equilibrium can be expected, confirmed that both types of IDBs each contained one monolayer of dopant ions.

In contrast, measurements in In-ZnO nanorods revealed boundary thickness $d \approx 0.27$ nm, corresponding to one close-packed monolayer of Fe$^{3+}$ (Figure 7). The trivalent oxidation state of Fe dopants was confirmed by Fe-L ELNES (energy-loss near-edge structure) analysis (Figure 8b), utilizing the valence-sensitive $L_3/L_2$ white-line intensity ratio [3].

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Figure 8a*

Table 1:

<table>
<thead>
<tr>
<th>Figure</th>
<th>Scan range (nm)</th>
<th>Number of (0002) layers</th>
<th>Number of basal IDBs</th>
<th>Number of pyramidal IDBs</th>
<th>Empty cation layers</th>
<th>Number of Zn layers</th>
<th>Ratio of cation layers</th>
<th>Equiv. one monolayer (at.%)</th>
<th>EDS analysis (at.%)</th>
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<tr>
<td>Figure 8a*</td>
<td>267</td>
<td>1027</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>847</td>
<td>Fe : Zn = 120 : 847</td>
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<td>13.5 (±0.5) Fe</td>
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<tr>
<td>Figure 9a**</td>
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<td>16</td>
<td>16</td>
<td>16</td>
<td>2442</td>
<td>In : Zn = 32 : 2442</td>
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<tr>
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<td>92</td>
<td>92</td>
<td>9693</td>
<td>In : Zn = 184 : 9693</td>
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<tr>
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<td>12</td>
<td>12</td>
<td>12</td>
<td>3618</td>
<td>In : Zn = 24 : 3618</td>
<td>0.66% In</td>
<td>1.2 (±0.2) In</td>
</tr>
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</table>

Table 1: Correlation between the number of inversion domain boundaries (IDBs) in STEM images and corresponding dopant concentrations as measured by EDS in STEM-SIX. * Sintered Fe-ZnO material; Fe₂O₃ : ZnO = 1 : 1.5. ** Sintered In-ZnO material. # Sintered In-ZnO material; large area scan (image not shown). ## In-ZnO nanorod grown by VLS method [4]. Section of nanorod shown in Figure 10.