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Iron Diffusion and Compound Formation in Zinc Oxide

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Highly charged ($z \geq 3$) transition metal ions are commonly added to zinc oxide (ZnO) to tune the electronic and optical properties in thin film applications. In recent years systems such as ZnO-Fe_2O_3 were studied, and it was found that homologous compounds with composition $Fe_2O_3(ZnO)_m$ exist besides the well-known zinc ferrite $ZnFe_2O_4$ [1]. In the present study we investigated the diffusion of Fe^{3+} into single crystals of ZnO using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and transmission electron microscopy (TEM). The diffusion samples consisted of thin films of Fe_2O_3 on *c* faces of ZnO crystals; the thin films were prepared by spin coating of an ethanolic solution of $Fe(NO_3)_3 \cdot 9H_2O$ and gentle heating. Diffusion experiments were performed by heating the samples at 1350 °C in a platinum-covered alumina crucible for different times.

Polished cross-sections of the diffusion samples were analysed by ToF-SIMS, with sub-micron lateral resolution [2]. Secondary ion intensity profiles were converted into concentration profiles by comparison with an appropriate (ion-implanted) standard. The resultant profiles are shown in Fig. 1a; they show plateaus of nearly constant Fe concentration, followed by sudden decreases at the diffusion front. The penetration depth increases from 46 to 108 μm with increasing time. Optical images of the cross-sections indicate a change in sample colour, from colourless to a yellowish brown colour, that corresponds exactly with extent of the Fe diffusion front (Fig. 1b). The concentration plateau of Fe is interpreted as a reaction zone of ZnO with Fe_2O_3 comparable with compound formation.

Scanning electron micrographs of etched side faces of the diffusion samples show roughening of the surface up to ca. 2/3 of the diffusion zone. From TEM analysis of cross-sections, a high density of inversion domains was observed at the sample surface, indicating the formation of a compound of composition $Fe_2O_3(ZnO)_m$ with small $m \approx 13$ (Fig. 2a). With increasing distance from the iron source the density of the inversion domains decreases, and at ca. 2/3 of the diffusion length no more inversion domains were found, in accordance with SEM results. High resolution elemental maps obtained by electron energy loss spectroscopy (EELS) reveal that the inversion domain boundaries contain one monolayer of Fe, as in the homologous compounds (see Fig. 3b) [3]. Hence, Fe is found predominantly at the inversion domain boundaries.

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TEM and X-ray spectroscopy (EDXS) of the Fe source-substrate interface established (i) that after short reaction times the Fe_2O_3 thin film has reacted to form zinc ferrite $ZnFe_2O_4$, which then acts as the source for further diffusion, and (ii) that the chemical composition at the diffused crystal surface has the average composition $Fe_2O_3(ZnO)_{13}$.

In summary, the incorporation of Fe^{3+} into ZnO leads to the formation of inversion domains with iron-decorated boundaries, up to depths of ca. 2/3 of the entire diffusion zone.

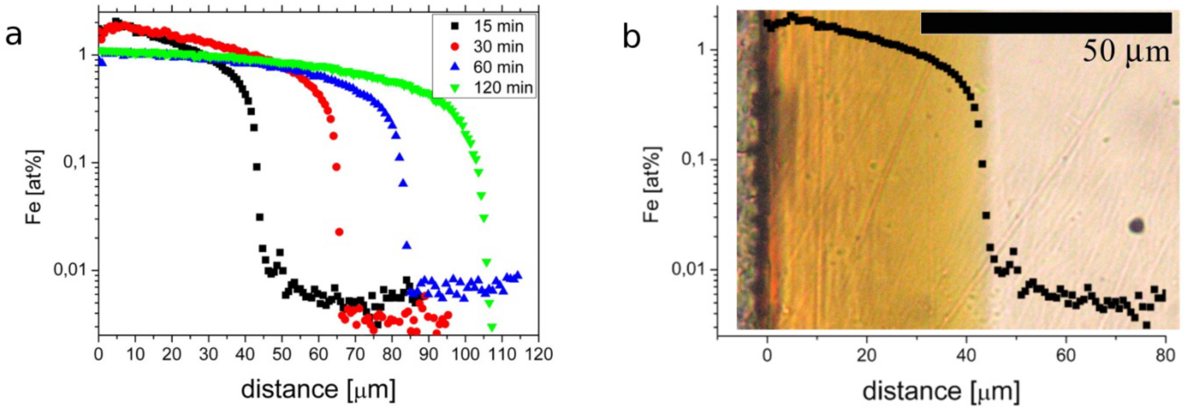

Fig. 1 (a) Fe concentration profiles determined by ToF-SIMS as a function of annealing time; (b). Optical image of ZnO crystal with Fe^{3+} diffusion zone (starting left) with Fe concentration profile after 15 min of diffusion.

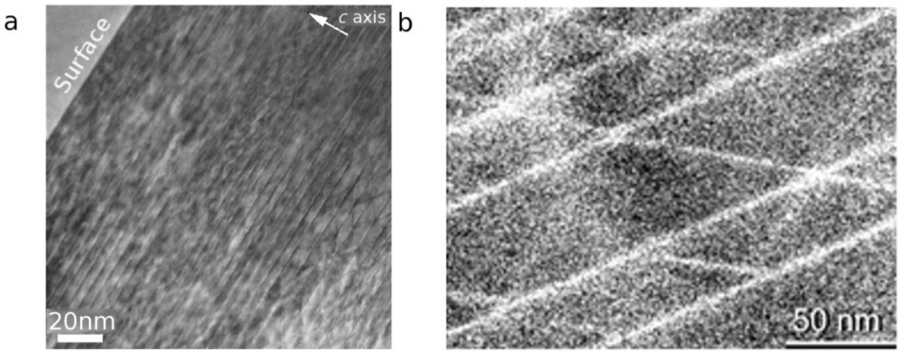

Fig. 2 (a) Domain microstructure at substrate surface; (b) iron distribution map proving Fe incorporation at domain boundaries.

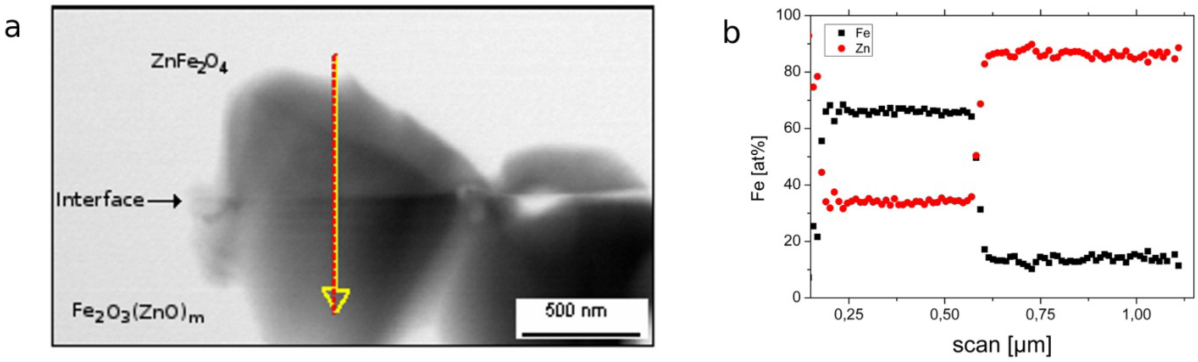

Fig. 3 (a) Bright field image of source-substrate interface and EDXS scan marked; (b) corresponding concentration profiles of Zn and Fe, proving a zinc ferrite source and $Fe_2O_3(ZnO)_{13}$ homologous phase formed in the substrate.

References

[1] N. Kimizuka, M. Isobe, M. Nakamura, T. Mohri, J. Solid State Chem. 103 (1993) 394.
[2] R. A. De Souza, M. Martin, Phys. Stat. Sol. (c) 4 (2007) 1785.
[3] W. Mader, O. Köster-Scherger, H. Schmid, N. Vanderschaeghe, F. Wolf, J. Am. Ceram. Soc. 90 (2007) 3984.

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