Aluminium-Substituted ZnO Thin Films: Thermoelectric Properties and Structural Characterisation

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Introduction and Motivation

Zinc Oxide as a Thermoelectric Material
- High Seebeck coefficient S for bulk material (-300 to -400 µV/K [1])
- Low production costs and non-toxicity
- High electrical resistivity ρ and thermal conductivity κ (10 Ωcm and 50 W/mK at RT [1])

Substituting Zinc with Aluminium: $Zn_{0.98}Al_{0.02}O$
- Lower electrical resistivity (ca 0.005 Ωcm from RT to 1000°C [1])
- Thermal conductivity still a drawback

Reducing Thermal Conductivity
- Lower dimensionality
- Morphology on nano-scale range and 2D thin films [2]

Synthesis

Magnetron Sputtering [3]:
- Radio-frequency (RF) method, plasma power 200 W
- Gas: mixture of Ar and Ar with 3% O_2
- Target: 2 wt% Al_2O_3-doped ZnO
- Deposition pressure: 10^{-3} mbar
- Deposition time: 16 min
- Substrate: Soda-lime glass
- Film thickness: 470 nm

Fig. 1: *Magnetron sputtering device.*

Morphology

Columnar grains:

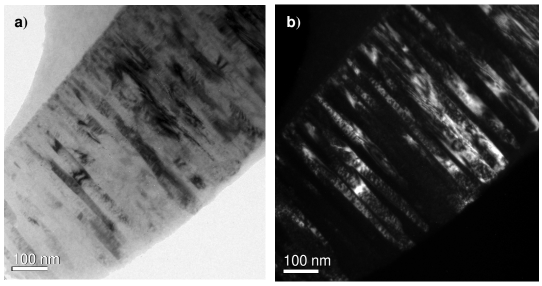

Fig. 2: *TEM images of as grown $Zn_{0.98}Al_{0.02}O$ thin films: a) BF, b) DF*
Film thickness th = 470 nm, grains ca 450 nm long and 15-35 nm wide.
The preferential orientation of the c-axis is perpendicular to the substrate.

Thermoelectric Properties

Abrupt change in thermoelectric properties when heating in air above around 640 K:

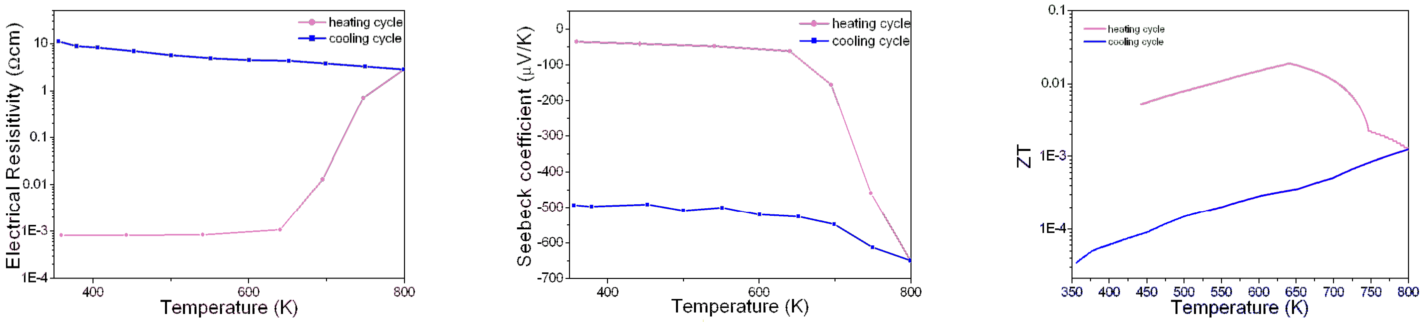

Fig. 6: *Thermoelectric properties of a $Zn_{0.98}Al_{0.02}O$ thin film. From left to right: 1) Electrical resistivity ρ(T), 2: Seebeck coefficient S(T), 3: Estimated ZT values as a function of the temperature calculated from the ρ(T) and S(T) from the thin film and an approximation of the thermal conductivity of a bulk sample from solid state reaction.*

Morphology and Crystal Structure with Temperature Treatment

Possible change in orientation with temperature:

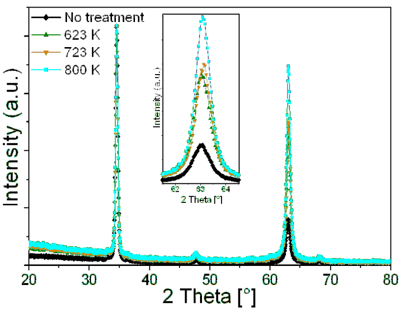

Fig. 3: *XRD patterns of $Zn_{0.98}Al_{0.02}O$ thin films measured after annealing treatment at different temperatures.*

Similar morphology before and after annealing treatment::

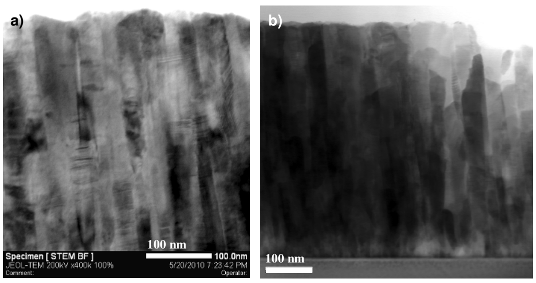

Fig. 4: *TEM images of $Zn_{0.98}Al_{0.02}O$ thin films: a) before annealing treatment, b) after annealing treatment at 800 K.*

But more different orientations after than before annealing treatment:

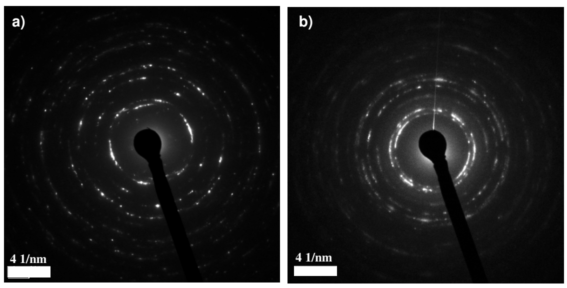

Fig. 5: *Electron diffraction of $Zn_{0.98}Al_{0.02}O$ thin films: a) before annealing treatment, b) after annealing treatment at 800 K.*

Conclusions

⇨The films show columnar grains with preferred orientation of the c-axis perpendicular to the substrate.

⇨ There is an abrupt change in the thermoelectric properties around 640 K.

⇨ The change could be due to the anisotropic character of the ZnO sample with a hexagonal structure ($\rho_{ab} \neq \rho_c$ [4]). The orientation of the grains change to more ab-plane contribution perpendicular to the substrate.

⇨ However, as the difference in the electrical resistivity before and after annealing treatment is large, the more reasonable explanation is due to a change in the oxygen content.

Outlook

⇨ More investigation on the grain orientation and the change in oxygen content with temperature will be done by TEM and by X-ray photoelectron spectroscopy (XPS).

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References

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